

# OBSERVING WINTER CARBONATE CHEMISTRY DYNAMICS THROUGHOUT THE MID-ATLANTIC BIGHT SHELF USING NOVEL GLIDER TECHNOLOGY

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## \* ABSTRACT

Increased atmospheric carbon dioxide ( $\text{CO}_2$ ) has led to global climate change and ocean acidification (OA) via the absorption of atmospheric  $\text{CO}_2$  by the ocean. Coastal shelves are also affected by various processes that influence the acidity of seawater, causing acidity to vary over time and space. These variations in ocean acidity can negatively impact marine species, especially calcifying organisms such as surfclams and sea scallops. In the Mid-Atlantic Bight (MAB), a subsection of the U.S. Northeast Shelf (NES), this variation in acidity generates ecological and economic concerns as the MAB is home to some of the nation's most productive and profitable estuaries and fisheries. In this study, Rutgers University (southern MAB) and Stony Brook University (northern MAB, Hudson Canyon) deployed two gliders equipped with sensors measuring depth, temperature, salinity, pH, dissolved oxygen, and chlorophyll to monitor winter 2021 carbonate chemistry conditions on the shelf as well as in slope waters of the MAB. For both deployments, measured pH and calculated aragonite saturation state ( $\Omega_{\text{arag}}$ ) showed opposing patterns, with high pH and low  $\Omega_{\text{arag}}$  in shelf/nearshore and low pH and high  $\Omega_{\text{arag}}$  in slope waters. These trends were attributed to different driving factors whereas pH was

more influenced by biological processes (i.e. photosynthesis) and  $\Omega_{\text{arag}}$  was influenced mostly by thermodynamics and chemical factors (i.e. temperature, total alkalinity). The results of this study underscore the importance of monitoring coastal acidity to understand potential impacts on important species.

**KEY TERMS:** ocean acidification, carbonate chemistry, glider, aragonite saturation state, pH, total alkalinity, Mid-Atlantic Bight, vertical mixing, Gulf Stream, Labrador Current

## COMMON TERMS AND ABBREVIATIONS

**MID-ATLANTIC BIGHT (MAB):** ocean region spanning just offshore from Cape Hatteras, NC to Martha's Vineyard, MA.

**COLD POOL:** mass of dense, cold bottom-water trapped due to stratification between surface and deep water during the late spring through summer months.

**ARAGONITE SATURATION STATE ( $\Omega_{\text{ARAG}}$ ):** calcium carbonate saturation state with respect to aragonite, measure for the potential of carbonate ions to form or dissolve;  $\Omega < 1$ : dissolve,  $\Omega > 1$ : form.

**TOTAL ALKALINITY (TA):** measure of the water's capacity to neutralize acids ( $\text{H}^+$  ions), measures the concentration of all alkaline ions (including carbonate and bicarbonate).

**OCEAN ACIDIFICATION (OA):** the increasing acidity levels of the ocean due to increased atmospheric  $\text{CO}_2$  absorption from anthropogenic  $\text{CO}_2$  emissions.

**PARTIAL PRESSURE  $\text{CO}_2$  ( $\text{pCO}_2$ ):** the pressure from carbon dioxide gas molecules; increasing  $\text{pCO}_2$  increases the solubility of carbon dioxide.

**SHELF:** region of shallower ocean water over the continental shelf (refer to [FIGURE 1](#)).

**IN-SLOPE:** deeper water just around shelf-break (the edge of shelf).

**ON SHELF:** water on the continental shelf.

**NEARSHORE:** water sampled closest to the shoreline, shallower water.

**U.S. NORTHEAST SHELF (NES):** a nearshore system with an extended shallow shelf.

**DISSOLVED INORGANIC CARBON (DIC):** total sum of inorganic carbon ( $\text{CO}_2$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ) in seawater.



**WATER-MIXING:** the mixing of surface and deeper water from wind-driven forces (waves).

**GLIDER:** autonomous underwater robots that sample continuously as they travel up and down through the water column along a programmed route (deployment refers to the initial release of a glider and recovery refers to the retrieval of the glider from the ocean).

**COASTAL DOWNWELLING:** surface water that is forced downward as wind moves it toward the coastal boundary which then becomes deep water that travels away from the coast.

**COASTAL UPWELLING:** deep water that is dragged up along the coast to replace surface water that was moved offshore by the wind.

**STRATIFICATION:** the separation of water column layers due to differing water densities and properties, typically observed in seasons with less ocean-mixing.

**THERMOCLINE:** a thin transition layer of water separating the surface and bottom water layers; due to the strong temperature differences between these layers, a rapid change in temperature is measured as one moves through the thermocline.

**EDDIES:** counter-current flow of water generating small whirlpools and circular movement of water.

**BUFFERING CAPACITY:** the ability of seawater to maintain a more neutral pH after being introduced to more acidic solutions, due to the concentration of salts and ions (such as  $\text{CO}_3^{2-}$ ) in seawater absorbing free-floating protons ( $\text{H}^+$ ).

## 1 INTRODUCTION

Anthropogenic activity, including the increased burning of fossil fuels and deforestation, has increased atmospheric carbon dioxide ( $\text{CO}_2$ ) and altered global climate and ocean conditions (IPCC, 2019). The increased rate of atmospheric  $\text{CO}_2$  absorption in the oceans, which results in complex chemical reactions that decrease seawater pH, has generated global concern over the acidification of ocean waters (Wanninkhof et al., 2015). Ocean acidification (OA) alters the balance of the carbonate system, including decreasing calcium carbonate saturation state in addition to the aforementioned decrease in pH. This presents a challenge for marine species by increasing physiological stress,

as they must increase energy expenditure on maintaining body structures or processes that depend on calcium carbonate stability. This specifically affects calcifying organisms such as sea scallops, which use carbonate to form their protective carbonate shells (Kroeker et al., 2013; Saba et al., 2019a). Seawater pH is projected to continue to globally decline over the next century, decreasing from the global average of 8.1 by 0.1-0.4 pH units (IPCC, 2019). This is expected to cause significant impacts on the health of ecosystems and play a role in the future distribution and range of species based on a species' tolerance to more acidic conditions.

### COASTAL PROCESSES INFLUENCING NEARSHORE CARBONATE CHEMISTRY

While ocean acidification is increasing globally at a relatively consistent rate, carbonate chemistry conditions of the seawater vary greatly across different spatial and temporal scales in nearshore coastal systems (Goldsmith et al. 2019). Nearshore waters experience these shifts due to various freshwater and terrestrial inputs, as well as mixing processes, which can alter the chemistry of the water (Wanninkhof et al., 2015; Goldsmith et al., 2019). For example, freshwater is naturally more acidic due to lower salinity and total alkalinity (TA) (Kwiatkowski & Orr, 2018). Additionally, photosynthesis and respiration can biologically alter carbonate chemistry, which increases and decreases pH, respectively. Respiration will dominate and increase partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) at deeper depths (Cai et al., 2011). Increased organic carbon and nutrients from rivers can lead to eutrophication of coastal systems and exacerbate this biological control on acidification (Anderson et al., 2002; Cai et al., 2011; Xu et al., 2020). Upwelling of deep,  $\text{CO}_2$  and nutrient rich water can support algal blooms and has previously been shown to result in increased acidity in the surface water (Anderson et al., 2002; DeGrandpre et al., 2002) seen along the U.S. west coast and seasonally off the coast of New Jersey. Water mass mixing, or a lack thereof, plays a significant role in controlling carbonate chemistry in coastal regions (Cai et al., 2020; Wright-Fairbanks et al., 2020). During

periods of strong stratification, a lack of mixing generates  $p\text{CO}_2$  rich bottom water and lower  $p\text{CO}_2$  surface water, creating vertical variation in carbonate chemistry. In contrast, well-mixed water columns have a relatively uniform  $p\text{CO}_2$ , meaning variation of carbonate chemistry is more minimal throughout the water column. In the northeast U.S., strong stratification begins in the spring and persists through summer when higher temperatures strengthen thermocline and prevent mixing, while high mixing occurs throughout the fall during seasonal overturn and persists into winter (DeGrandpre et al., 2002; Wright-Fairbanks et al., 2020).

#### INFLUENCE OF CURRENTS AND SEASONALITY ON CARBONATE CHEMISTRY

The two major currents that influence the chemistry of the U.S. Northeast Shelf (NES) and slope water are the Labrador Current and Gulf Stream (FIGURE 1). The Labrador Current is a cold, fresher current that transports water southward from the Nova Scotia region to the Mid-Atlantic Bight (MAB). This colder, less alkaline water allows

for more  $\text{CO}_2$  absorption, leading to lower calcium carbonate saturation state with respect to aragonite ( $\Omega_{\text{arag}}$ ). The Gulf Stream is a warm, salty current that transports water northward from the Gulf of Mexico along the coastline, diverging offshore at the edge of the MAB near Cape Hatteras, NC. Compared to the Labrador Current, it is characterized by a high  $\Omega_{\text{arag}}$  and TA. Overall, these two opposing currents influence the carbonate chemistry of the Northeast Shelf through mixing of waters with different  $\text{CO}_2$  buffering capacities (Wanninkhof et al., 2015; Xu et al., 2020). Along with the influence of these currents, the aforementioned mixing processes and coastal influences drive spatial and temporal variations in NES seawater carbonate chemistry. High summer temperatures generate a strengthened thermocline leading to a highly stratified water column. This warmer, less dense surface water lays on top of a bottom layer of colder fresher water – most likely originating from the Labrador Current – which becomes confined underneath by the density difference. This trapped

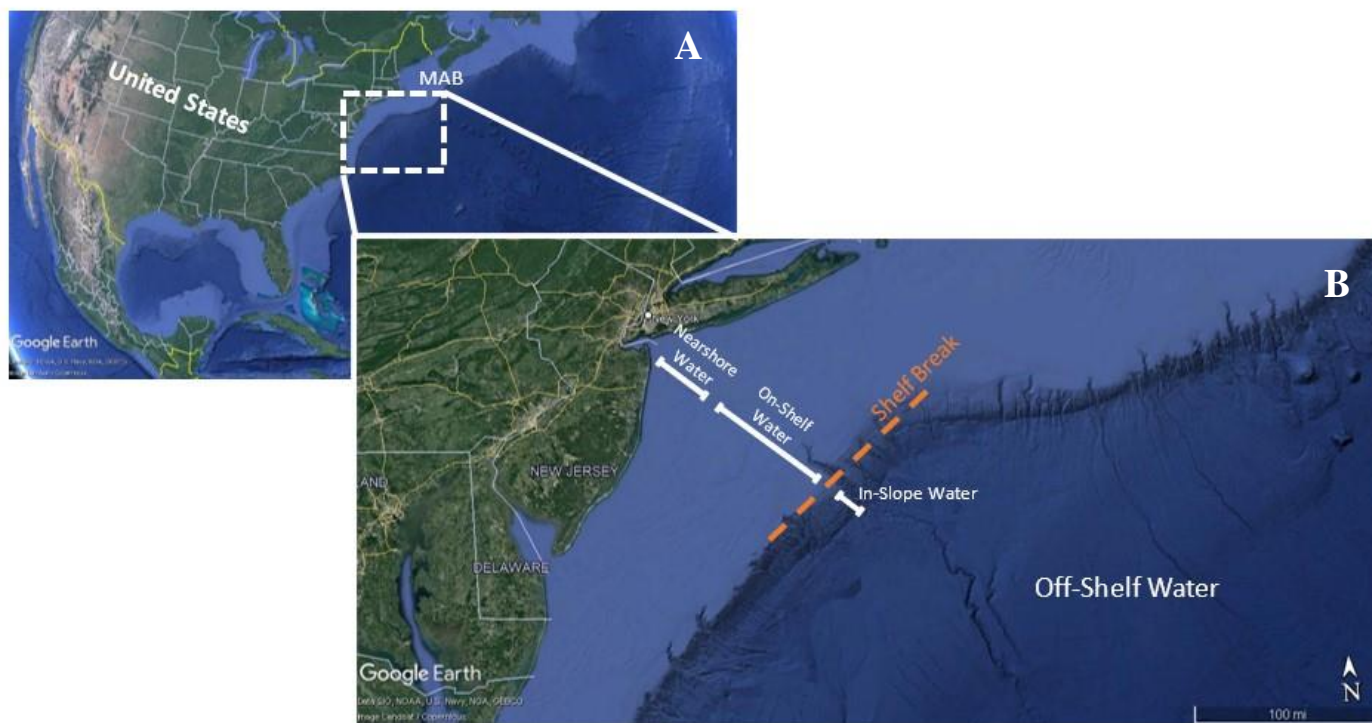


FIGURE 1: (A) Map of the NES, white box highlighting the MAB. (B) Map focused in on the MAB area, illustrating concept of nearshore, on-shelf, and in-slope water.

cold, fresher water mass creates a unique shelf feature specific to the MAB referred to as the “Cold Pool,” and its presence or absence (based on the degree of mixing) can impact the carbonate chemistry throughout the water column. With the formation of the Cold Pool during the summer months, a pocket of high pCO<sub>2</sub> is contained at the shelf floor, creating a stark difference in carbonate chemistry between the Cold Pool water and the lower pCO<sub>2</sub> water of the rest of the water column (Wright-Fairbanks et al., 2020).

#### ECONOMIC AND ECOLOGICAL SIGNIFICANCE

It is important to note that these coastal processes and their seasonal cycles are not well studied on a regional scale, and therefore the effects of seasonal variation regarding OA and the impacts on ecosystem health along the NES are not well understood either (Xu et al., 2020). However, studies on OA and understanding coastal variations are important, especially for coastal fisheries. The NES supports many of the nation’s most productive and valued commercial fisheries (National Marine Fisheries, 2021). Atlantic sea scallops (*Placopecten magellanicus*) and Atlantic surfclams (*Spisula solidissima*) are both calcifying organisms that rely on carbonate molecules to develop their shells; these important Atlantic fisheries generate \$569.9 million and \$30.7 million, respectively (National Marine Fisheries, 2021). Shellfish like scallops and surfclams that inhabit low carbonate environments (Hart et al., 2004; Wanninkhof et al., 2015; Pousse et al., 2020) can be at increased risk of mortality from predation with acidification, causing shell deformities and weaker shells (reviewed in Saba et al., 2019a).

#### GLIDERS

Due to the dynamic nature of coastal systems and their importance in economically productive fisheries, it is critical to monitor and understand OA and carbonate chemistry. This is especially urgent as climate change is predicted to generate a global trend of increased acidity. High-resolution data collected over short-term, or seasonal, time periods can help to construct a better understanding of the effects of the different coastal processes on

acidity trends along the Northeast Shelf (Xu et al., 2020; Xu et al., 2017; Wanninkhof et al., 2015; Wright-Fairbanks et al., 2020). Gliders are autonomous underwater vehicles that can be equipped with various sensors, including the recently developed pH sensor, enabling continuous pH measurements to be taken throughout their deployments. Gliders travel off shelf and back to shore, continuously taking measurements while climbing up and down through the water column, providing high-resolution observations of the shelf. Glider science sensors sample at a rate of 0.5 Hz, resulting in interval measurements of every 20-30cm vertically producing these high-resolution datasets (Saba et al., 2019b; Wright-Fairbanks et al., 2020). This ability to provide high-resolution data and cross-sectional perspectives of the water column makes gliders ideal for monitoring OA and carbonate saturation along the Northeast Shelf (Saba et al., 2019b). Rutgers University continues to use pH gliders to conduct seasonal surveys of the shelf to investigate carbonate chemistry dynamics as well as to map potential hot spots and time periods of acidification in important fisheries’ habitats. The purpose of my research project is to examine shelf-wide winter carbonate chemistry dynamics using data collected from two pH glider deployments conducted in the northern and southern MAB.

## 2 MATERIALS AND METHODS

Data collection and analysis methods followed those used in seasonal surveys described in Wright-Fairbanks et al. (2020). The winter 2021 surveys were conducted as a collaborative effort between Rutgers University (southern MAB deployment) and Stony Brook University (northern MAB deployment). Teledyne-Webb Slocum G2 gliders were deployed in each MAB site during similar timeframes. Both gliders were deployed on February 26, 2021. The Rutgers University glider was recovered on March 21, 2021, and the Stony Brook University glider was recovered on March 23, 2021, with missions lasting about 24 and 25 days respectively (FIGURE 2A). The Rutgers University glider was deployed and recovered out of Tuckerton, NJ (FIGURE 2A - ROUTE R), and the Stony Brook University

glider was deployed out of Shinnecock Inlet, NY and recovered out of Manasquan, NJ (FIGURE 2A - ROUTE S). Each glider was equipped with a recently developed deep-ISFET pH sensor (Saba et al., 2019b) as well as CTD (conductivity, temperature, and pressure/depth), an Aanderaa optode measuring dissolved oxygen (DO), and an optics puck measuring chlorophyll fluorescence and spectral backscatter. Further details on the specific procedures for preparation, deployment, and recovery of gliders is outlined in Wright-Fairbanks et al. (2020). During deployment and recovery, discrete water samples were collected and sent to a lab at the University of New Hampshire for chemical analysis for the purpose of ground-truthing glider pH and carbonate parameter data (Wright-Fairbanks et al., 2020). This validation sample analysis is still ongoing.

Data collected by the gliders were converted using Slocum Power Tools (Kerfoot, 2014) into a format for data analysis using MATLAB software (version R2021a). Analysis techniques described in Wright-Fairbanks et al. (2020) were applied to the data collected from these winter 2021 deployments and included sensor response time shift calculations and application to the full dataset, data quality assurance and quality control (QA/QC), estimating TA-salinity regression relationships to calculate TA, calculation of the full suite of carbonate chemistry parameters (pH, TA:DIC,  $\Omega_{\text{arag}}$ ) (using CO2SYS v3.0 in MATLAB), binning parameter data by depth and distance/time, plotting parameters, and running statistical analyses/tests on the full quality-controlled dataset. Methods for this step-wise analysis are described in detail below.

Sensor time lag can occur because temperature measurements are taken external to the CTD conductivity cell while conductivity measurements, used for calculating other variables including salinity and TA, are taken within the cell. This separation can cause a "thermal lag" where temperature measurements misalign and generate offset measurements (Saba et al., 2019b). To account and correct this thermal lag, different potential time shifts from 0 to 60 seconds (at 1 second intervals) were run on paired upcast/downcast data, and average time

shift for the entire deployment was applied to dataset (Wright-Fairbanks et al., 2020). Once time shift was applied, QA/QC tests (gap test, syntax test, location test, gross range test, and spike test) were run on the glider dataset to assess the data for any "bad" data points (outlying, incredibly deviated points) created from sensor failure/malfunction and remove if present (further detailed in IOOS, 2019). Because discrete sample analysis is ongoing, we were unable to construct a deployment-specific linear regression model of TA as a function of salinity. Instead, a previous winter deployment (2019) TA-salinity relationship was used to derive regression coefficients for calculating TA values, meaning slight variations in TA values between true calculations (if values were calculated using 2021 discrete samples) and calculated are possible. The previous winter deployment used to calculate TA values lasted a duration of 19 days, from February the 1st to the 19th, 2019, and was deployed offshore Sandy Hook, NJ maintaining a course in the MAB in between the glider tracks of the winter 2021 deployments (Wright-Fairbanks et al., 2020). This refined data set was then used to calculate carbonate chemistry parameters using CO2SYS for MATLAB (v3.0) (Lewis & Wallace, 1998; Sharp et al., 2020; van Heuven et al., 2011; Wright-Fairbanks et al., 2020). Following this, the data were then binned by time (1-hour bins) to generate a series of profiles of the measured or calculated parameters over depth (m) and time (hours). These parameters included: temperature ( $^{\circ}\text{C}$ ), salinity (PSU), dissolved oxygen (mg/L), chlorophyll ( $\mu\text{g/L}$ ), pH, TA ( $\mu\text{mol/kg}$ ), and  $\Omega_{\text{arag}}$ . To further understand and visualize the data, in addition to the depth profiles, 3-dimensional cross-section models of the shelf were constructed. Finally, statistical analyses were conducted to determine significance ( $p < 0.05$ ) of data spread and the relationships between parameters via correlation coefficients (Wright-Fairbanks et al., 2020). Correlation coefficients were calculated using MATLAB package "Statistics and Machine Learning Toolbox," version 2021a, and tables for both datasets for carbonate parameters were generated using Microsoft Excel (2008) and the conditional formatting function.

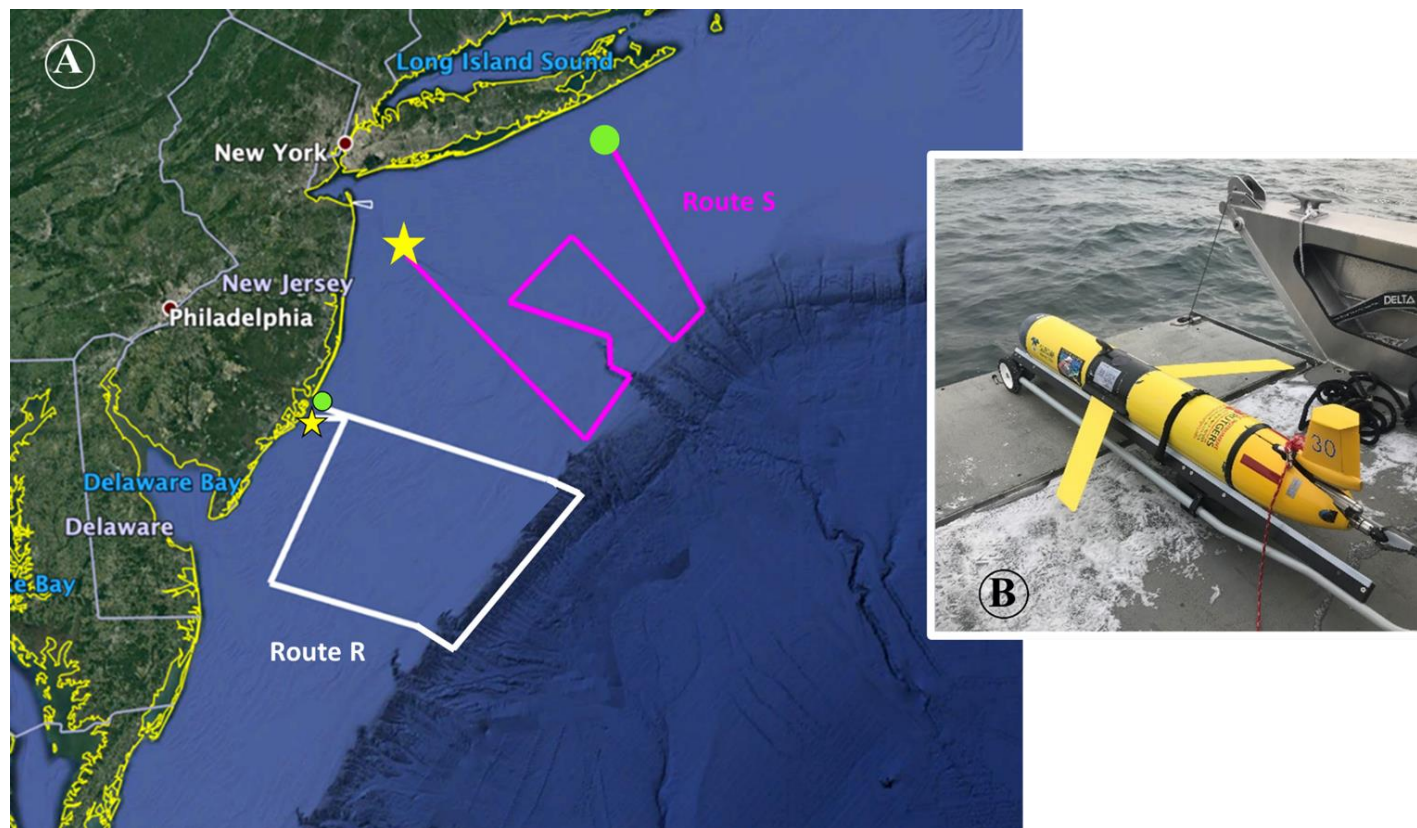


FIGURE 2: (A) Maps illustrating glider mission tracks for the winter 2021 survey along NES. (Route R) Glider tracks for MAB deployment (white) (star = recovery site, green dot = deployment site). (Route S) Glider tracks for Hudson Canyon deployment (magenta) (star = recovery site, green dot = deployment site). (B) At right, photography of Rutgers glider (RU 30) being deployed (Photo credit: Elizabeth Wright-Fairbanks).

### 3 RESULTS

#### GLIDER DATA

Both glider missions exhibited similar trends in both chemical and physical parameters. Temperatures above 12 °C and salinities above 35 PSU were observed offshore/in-slope waters, while lower temperatures (below 8 °C) and salinities (below 33 PSU) were observed nearshore (FIGURE 3 A, B; FIGURE 4 A, B). Higher dissolved oxygen (above 9.5 mg/L) and chlorophyll (above 2 µg/L) concentrations were observed nearshore and along shelf, while lower concentrations for both (below 7.5 mg/L; below 1 µg/L) were observed at the shelf break and in-slope water (FIGURE 3 C, D; FIGURE 4 C, D). Looking at carbonate chemistry parameters, pH was lower (7.95 – 8) in deeper in-slope water, while pH was higher (8.1-8.15) on shelf (FIGURE 3 E; FIGURE 4 E). Higher TA (2300-2350 µmol/kg) and  $\Omega_{arag}$  (2.4 – 2.6)

were observed at the shelf break and in deeper in-slope water and lower TA (below 2250 µmol/kg) and  $\Omega_{arag}$  (below 2) were observed nearshore and on the shelf (FIGURE 3 F, G; FIGURE 4 F, G). Prevalent mixing of the water column and uniform surface and bottom waters on the shelf were also observed in both glider datasets.

Unique oceanographic features were evident in the Rutgers glider dataset (FIGURE 3). Past the shelf break, significant water column mixing was reflected in all profiles (3/6 – 3/9), in the upper 200 m where the glider sampled. Additionally, when the Rutgers glider was returning to the shelf (3/11 – 3/12) on the southernmost transect, a pocket of elevated chlorophyll (3 µg/L) was noted to coincide with elevated pH (8.15; FIGURE 3E) and  $\Omega_{arag}$  (2.4; FIGURE 3G).

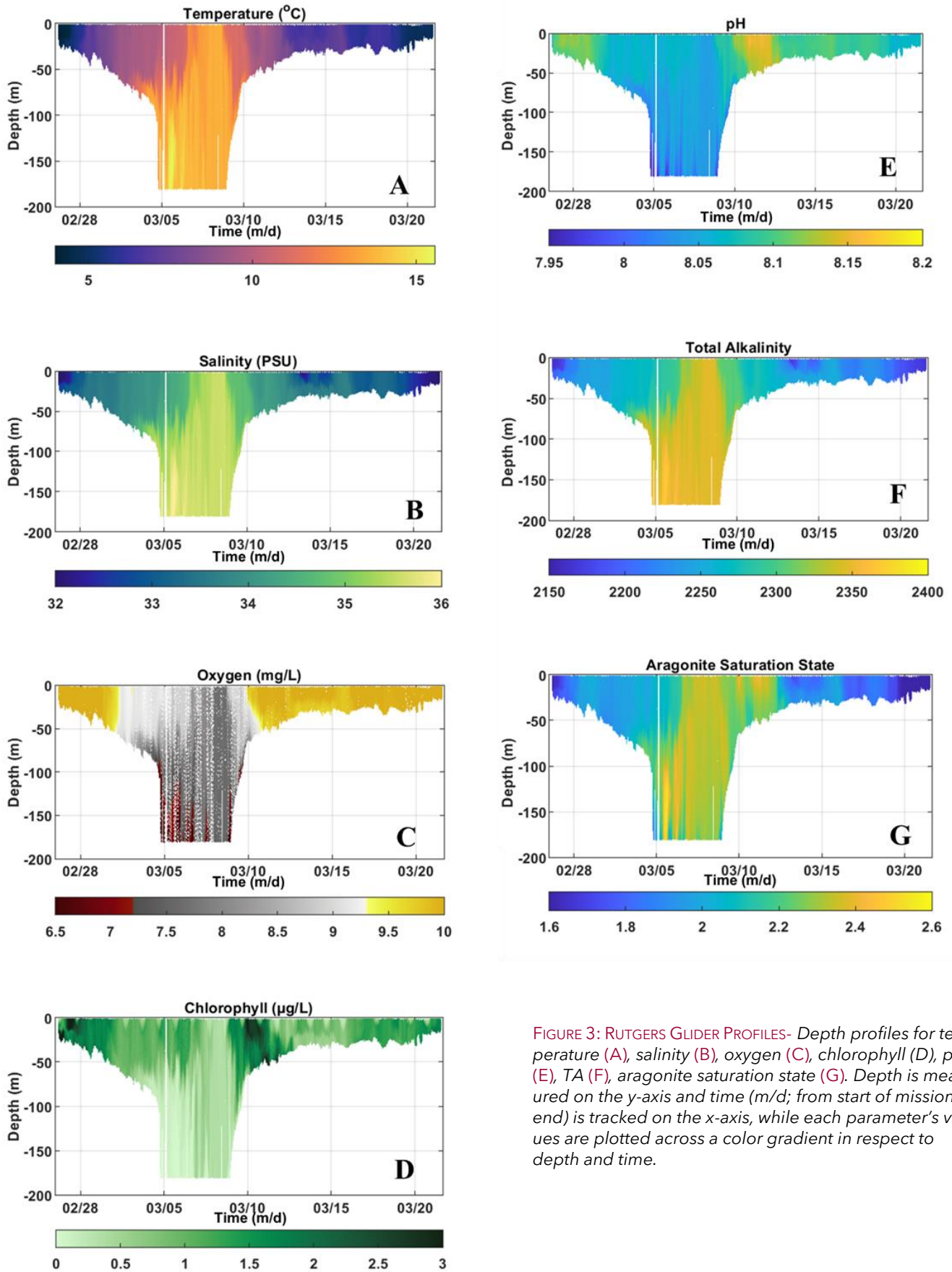


FIGURE 3: RUTGERS GLIDER PROFILES- Depth profiles for temperature (A), salinity (B), oxygen (C), chlorophyll (D), pH (E), TA (F), aragonite saturation state (G). Depth is measured on the y-axis and time (m/d; from start of mission to end) is tracked on the x-axis, while each parameter's values are plotted across a color gradient in respect to depth and time.

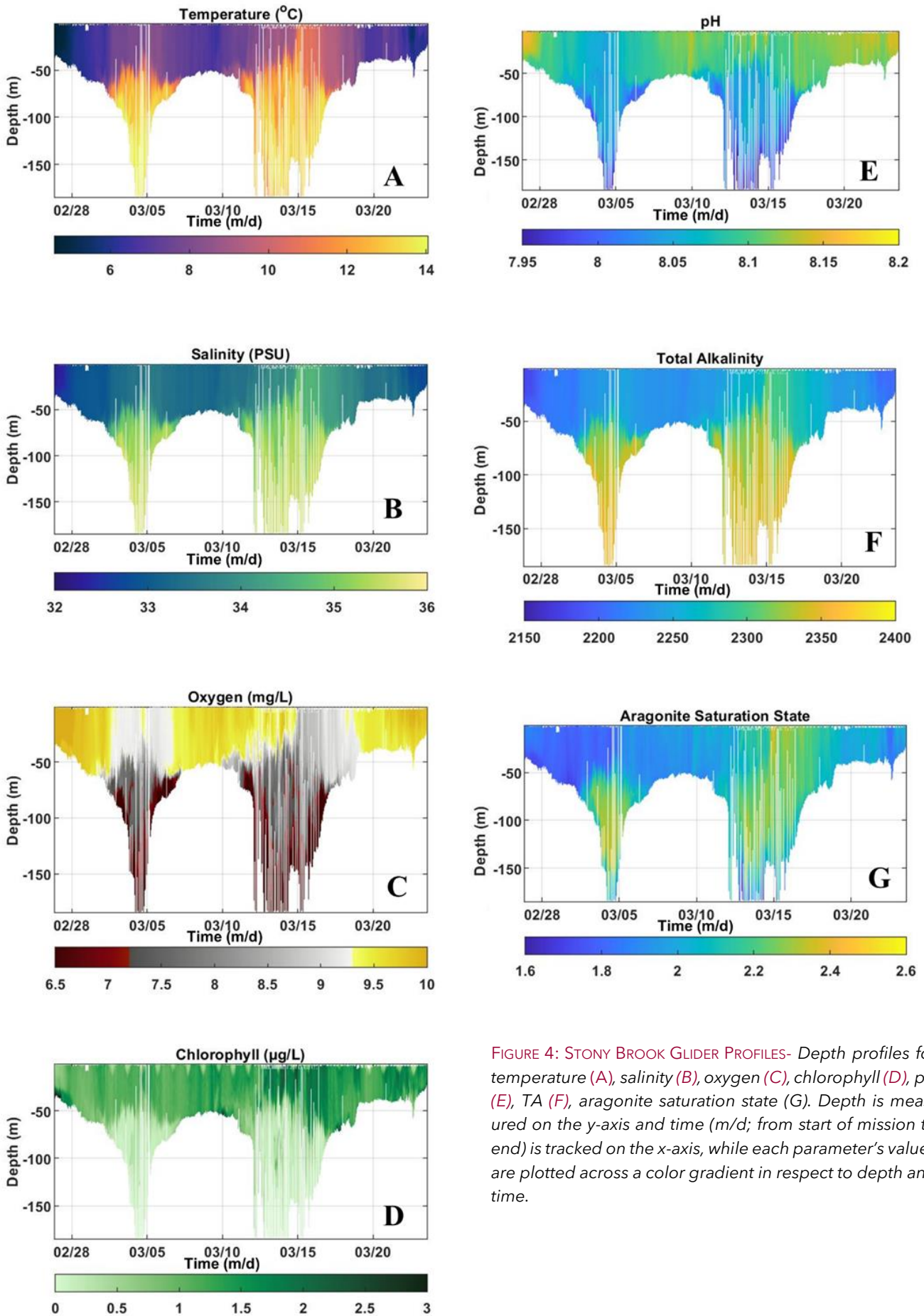


FIGURE 4: STONY BROOK GLIDER PROFILES- Depth profiles for temperature (A), salinity (B), oxygen (C), chlorophyll (D), pH (E), TA (F), aragonite saturation state (G). Depth is measured on the y-axis and time (m/d; from start of mission to end) is tracked on the x-axis, while each parameter's values are plotted across a color gradient in respect to depth and time.



EXAMINING THE RELATIONSHIP BETWEEN pH AND  $\Omega_{\text{arag}}$

Similar patterns in the relationship between pH and  $\Omega_{\text{arag}}$  relative to temperature and salinity were observed with both gliders (FIGURE 5). For pH, higher values occurred at higher temperature and salinity, while lower pH values were associated with lower temperature and salinity values (FIGURE 5 A, B). The opposite pattern was observed with  $\Omega_{\text{arag}}$ , where low values occurred at low temperature and salinity, while high values were observed at high temperature and salinity (FIGURE 5 C, D).

To understand the drivers behind the pH and  $\Omega_{\text{arag}}$ , the correlation coefficient tables (Tables 1, 2) were used. For both datasets, pH had the strongest positive correlation with oxygen concentrations (0.73; 0.78) and, unlike  $\Omega_{\text{arag}}$ , had a stronger positive correlation with chlorophyll concentration (0.59) as well. While  $\Omega_{\text{arag}}$  had the strongest positive correlation with salinity and TA (0.94; 0.83), both pH and  $\Omega_{\text{arag}}$  had a stronger correlation to temperature. The pH had a negative relationship with temperature (- 0.56; - 0.70) while  $\Omega_{\text{arag}}$  had a stronger positive

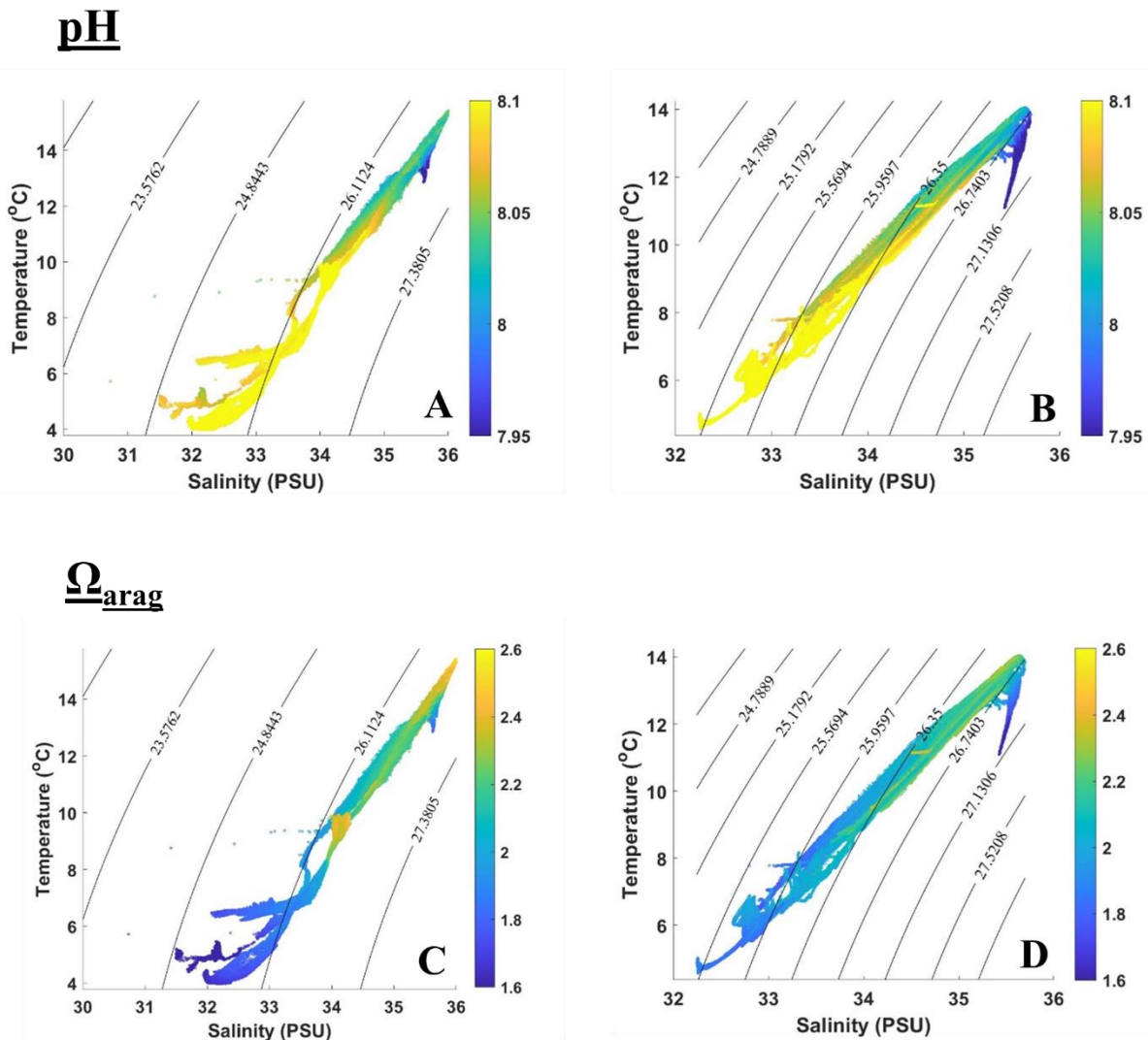
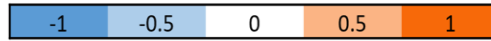


FIGURE 5: Temperature-Salinity plots for pH (top) and aragonite saturation state (bottom) for both Rutgers (A, C) and Stony Brook (B, D) gliders. Temperature is measured on the y-axis and salinity is measured on the x-axis, lines representing isopycnals (points of specific water densities) overlaid to give visuals of ocean water layering. Parameter of interest values plotted across a color gradient in respect to temperature and salinity.

<b>Rutgers</b>				<b>Stony Brook</b>			
	<b>pH</b>	<b>TA</b>	<b>Arag</b>		<b>pH</b>	<b>TA</b>	<b>Arag</b>
pressure	-0.48	<b>0.68</b>	<b>0.54</b>	pressure	<b>-0.67</b>	<b>0.57</b>	0.31
temperature	<b>-0.56</b>	<b>0.98</b>	<b>0.91</b>	temperature	<b>-0.70</b>	<b>0.98</b>	<b>0.78</b>
salinity	-0.48	1*	<b>0.94</b>	salinity	<b>-0.63</b>	1*	<b>0.83</b>
chlorophyll	<b>0.59</b>	-0.49	-0.34	chlorophyll	<b>0.59</b>	-0.35	-0.12
oxygen	<b>0.73</b>	<b>-0.88</b>	<b>-0.72</b>	oxygen	<b>0.78</b>	<b>-0.94</b>	<b>-0.67</b>
latitude	0.17	<b>-0.72</b>	<b>-0.75</b>	latitude	0.32	<b>-0.86</b>	<b>-0.81</b>
longitude	<b>-0.64</b>	<b>0.68</b>	<b>0.56</b>	longitude	<b>-0.57</b>	0.04	-0.26
pH	1.00	-0.48	-0.23	pH	1.00	<b>-0.63</b>	-0.18
TA	-0.48	1.00	<b>0.94</b>	TA	<b>-0.63</b>	1.00	<b>0.83</b>
$\Omega_{arag}$	-0.23	<b>0.94</b>	1.00	$\Omega_{arag}$	-0.18	<b>0.83</b>	1.00



**Correlation Coefficient Color Gradient Scale**

**TABLES 1 AND 2:** Correlation coefficients for both Rutgers (left) and Stony Brook (right) glider data for the different carbonate parameters (pH, TA,  $\Omega_{arag}$ ). All coefficients were significant ( $p < 0.05$ ). Coefficient values greater than |0.5| (in bold) indicate stronger correlation. Orange shaded cells = positive correlation, blue shaded cells = negative correlation; increased color saturation indicates increased correlation. \*TA calculated as a function of glider salinity values, therefore coefficient of 1.

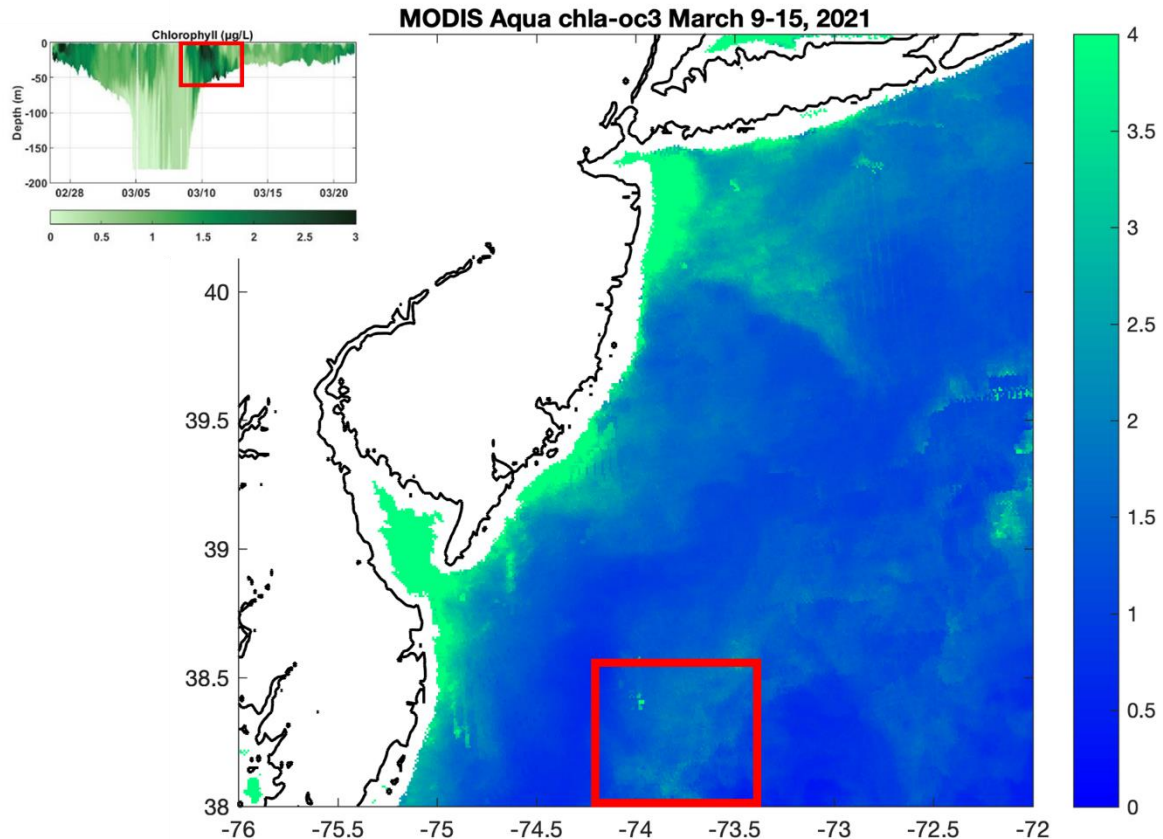
relationship with temperature (0.91; 0.78). Finally, TA had the greatest positive correlations to temperature (0.98) and  $\Omega_{arag}$  (0.94; 0.83) as well as strong negative correlations with oxygen (-0.88; -0.94) and latitude (-0.72; -0.86). These trends in the correlation coefficients and drivers for the carbonate parameters align with patterns of high/low values of related parameters, such as salinity and chlorophyll, observed by the gliders in nearshore/on shelf and in-slope waters.

#### 4 DISCUSSION

In this study, two sets of glider data provided by Rutgers University (southern Mid Atlantic Bight) and Stony Brook University (northern Mid Atlantic Bight/Hudson Canyon) illustrated carbonate chemistry patterns in the MAB. Over the course of the winter 2021 mission, pH and  $\Omega_{arag}$  varied across time and space from the influences of biological, chemical, and physical processes. This glider data can then be related to commercial fishery management zones, particularly shellfish fisheries, to understand the potential responses of marine animals to acidification.

#### IMPACT OF CURRENTS ON PARAMETER PROFILES

Depth profiles of in-slope waters of both deployments suggest direct influence from the warmer, saltier Gulf Stream that produced higher temperature and salinity conditions, similar to those observed during a previous winter glider deployment in the MAB (Wright-Fairbanks et al., 2020). These warmer, more saline conditions acted as drivers for high TA and  $\Omega_{arag}$  values in deep in-slope waters for both datasets and surface in-slope waters for Rutgers deployment. The spatial variation in  $\Omega_{arag}$  values, with higher values seen in Rutgers (southern) compared to Stony Brook (northern) deployment, is consistent with the “south-to-north decline” of  $\Omega_{arag}$  described in Cai et al. (2020) from the weakening influence of highly saturated and buffered Gulf Stream water. The Gulf Stream carries warmer saltier water from the tropics, which in effect has a lower DIC/TA ratio, thus increasing the buffering capacity of the water maintaining higher  $\Omega_{arag}$  (Cai et al., 2020; Wright-Fairbanks et al., 2020). This northward current traveling alongside the shelf can be pushed up onto and mix with shelf waters via warm-core eddies (Fratantoni et al., 2001; Zhang et al., 2015;



**FIGURE 6:** Satellite data for surface chlorophyll concentrations in the southern MAB (3/9 - 3/15) (NASA Goddard Space), red box indicating area Rutgers glider traveling through during same timeframe. Rutgers glider chlorophyll data (top left) included for comparison, red box indicating elevated chlorophyll concentration of interest.

Wright-Fairbanks et al., 2020) and consequently lead to high TA and  $\Omega_{\text{arag}}$ , which was especially notable in the more southern Rutgers dataset.

Conversely, nearshore shelf waters were generally colder and fresher, influenced both by coastal freshwater input and potentially the southward flowing Labrador Current (Xu et al., 2017; Wright-Fairbanks et al., 2020). These fresher and shallow depth conditions of nearshore and shelf water were also characterized by higher chlorophyll and oxygen concentrations, the latter of which was likely a function of both higher productivity (i.e., oxygen production through photosynthesis) and cold-water temperatures (i.e., increased gas solubility). Furthermore, these nearshore and shelf conditions translated to high pH and low TA and  $\Omega_{\text{arag}}$  values, which is consistent with observations from the previous winter survey Wright-Fairbanks et al. (2020).

The high observed pH values can be potentially attributed to the influence of increased biological uptake of  $\text{CO}_2$  via increased photosynthesis in shallower shelf and nearshore water (Cai et al., 2020; Wright-Fairbanks et al., 2020).

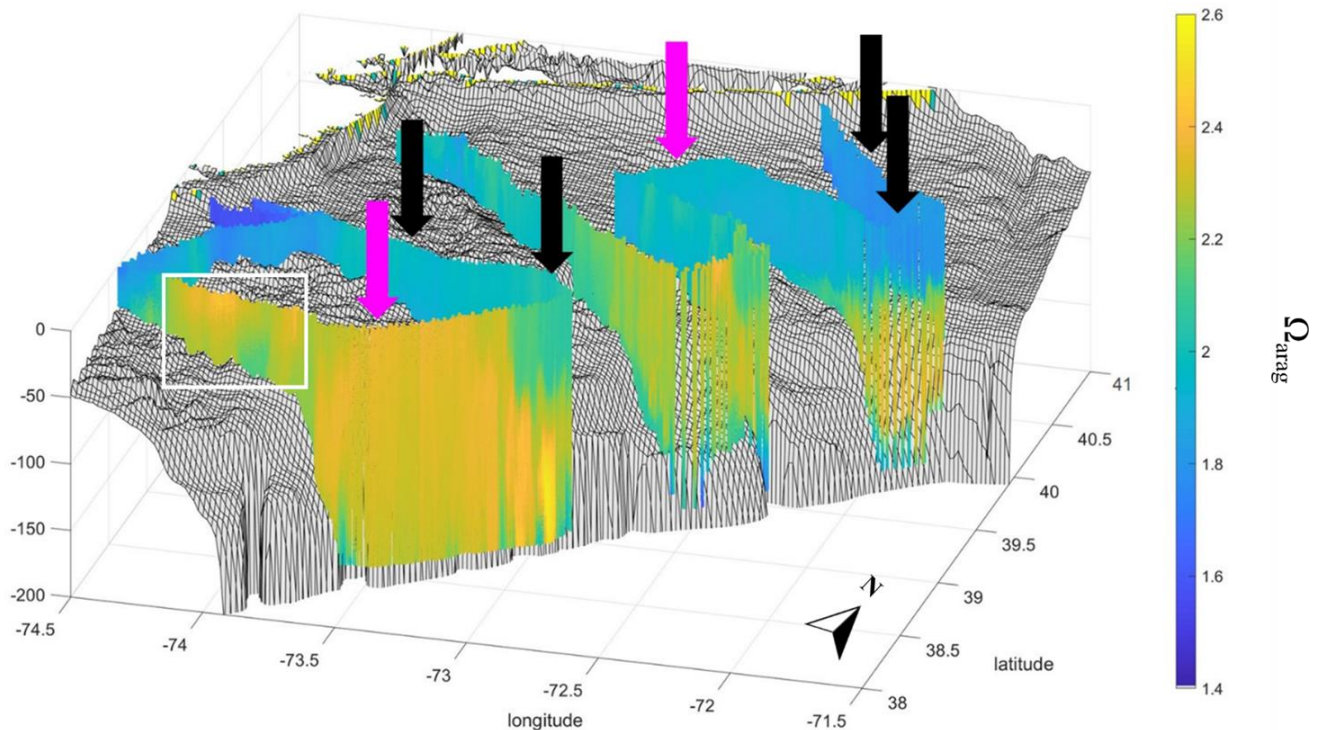
#### PH AND $\Omega_{\text{ARAG}}$ DRIVERS

The significant strong correlations of pH with chlorophyll and oxygen indicate that pH was more directly driven by biological influences, such as photosynthesis-respiration rates. Conversely,  $\Omega_{\text{arag}}$  was more so driven by physical and chemical influences, such as currents and water temperature, with significant strong correlations to TA, salinity, and temperature. This supports the conclusions of Cai et al. (2020), who found that  $\Omega_{\text{arag}}$  is temperature-driven in the coastal western Atlantic while pH is

more susceptible to short-timescale drivers like phytoplankton blooms.

The drivers of pH and  $\Omega_{\text{arag}}$  are further understood by looking at the unique, event-based features that occurred during the Rutgers glider mission (FIGURE 3). On the southern-most transect, as the glider returned on shelf (3/11 - 3/12), a pocket of both high pH and elevated chlorophyll was observed (FIGURE 3 D, F). Satellite data from the same timeframe (FIGURE 6) confirmed the elevated glider chlorophyll measurements, supporting the fact that biological interactions – specifically photosynthesis rates – have a large impact on pH values. Additionally, the direct relationships between  $\Omega_{\text{arag}}$  and TA, salinity, and temperature were evident on the southern-most transect (3/11 - 3/12; FIGURE 3), likely due to a storm-driven “sloshing event.” During early March strong and variable wind events, such as Nor’easters and South/West winds, were observed within the

glider data and promoted water column mixing and shifting currents (FIGURE 7). Earlier Nor’easters (3/1, 3/5) produced strong northeast winds that traditionally promote downwelling of shelf waters due to the buildup of water along the coast. Strong South and West winds beginning on 3/9 likely caused currents to shift in the opposite direction and potentially promoted a switch to intrusion of high  $\Omega_{\text{arag}}$  in-slope water onto the shelf. These events further support that  $\Omega_{\text{arag}}$  was more impacted by physical influences; in this case,  $\Omega_{\text{arag}}$  was driven by wind-driven mixing. It is important to acknowledge that this is an observational study for an area of research where limited experimental studies have been conducted, limiting the ability to predict which variables drive pH and  $\Omega_{\text{arag}}$  changes the most. The scarcity of experimental studies leaves opportunities for researchers to expand on our understanding of the drivers of pH and



**FIGURE 7:** 3D glider transects for  $\Omega_{\text{arag}}$ , Rutgers glider tracks (south) and Stony Brook (north), with shelf floor bathymetry and northeast coastline (drawn around long. -74.5) illustrated. Black arrows = Nor'easter (northeast winds, winds promoting downwelling on shelf water); magenta arrows = South and West winds (winds triggering shift to upwelling of offshore/in slope water). White box area of interest highlighting potential sloshing event from shifting currents.

$\Omega_{\text{arag}}$  through controlled experiments in which significantly correlated parameters (oxygen and chlorophyll concentrations, temperature, etc.) are manipulated individually.

#### STRONG WINTER MIXING EVENT

In any given depth profile nearshore or on the shelf, the water column was fully mixed, as is typical for MAB winter conditions (Castelao et al., 2010). Stratification of in-slope waters occurred during the early part of the deployment (early March) but disintegrated over time, likely due to increased storm-related winds. This event was most pronounced in the southern (Rutgers) dataset where strong mixing of the water column was observed (3/6 - 3/9) within deeper in-slope water, revealing full water column homogenization for the maximum depth sampled (200m) (FIGURE 3). This was the first time this degree of slope water mixing event has been observed in a Rutgers winter survey. This mixing event highlights the prevalence of interannual variability of the Gulf Stream-influenced shelf break jet in the MAB, which has been described by Linder (1996) and Linder and Gawarkiewicz (1998). Typically, the shelf break jet is more stratified for in-slope waters due to differing salinities between denser, saltier Gulf Stream water and fresher overlaying surface water in the winter, which was seen in the Stony Brook deployment (FIGURE 4) (Linder & Gawarkiewicz, 1998). However, in the Rutgers deployment, the described stratification of water masses of the winter shelf break jet was not present during 3/6 - 3/9, and instead a uniform, unstratified shelf break jet from full column (200 m) mixing was observed (FIGURE 3).

#### SIGNIFICANCE

To stress the significance and importance of monitoring carbonate chemistry in coastal systems, it is important to relate this data to further biological and economic implications. Atlantic surfclams and Atlantic sea scallops are both calcifying organisms that reside in and are major fisheries of the MAB (National Marine Fisheries, 2021). Atlantic surfclams reside nearshore in waters of 10-50m in depth

(Pousse et al., 2020), while Atlantic sea scallops inhabit mid- to outer-shelf waters 27-80m deep (Hart et al., 2004). Referring back to the  $\Omega_{\text{arag}}$  plots (FIGURE 7, FIGURE 3G, FIGURE 4G), the observed glider data in these essential habitat regions highlight that in winter surfclams are exposed to relatively lower  $\Omega_{\text{arag}}$  while sea scallops inhabit waters with higher  $\Omega_{\text{arag}}$  due to greater influence from the Gulf Stream. The difference in habitat range between these species, along with the natural variation in  $\Omega_{\text{arag}}$  across the shelf, is important for understanding which species may be more impacted with ongoing ocean acidification and episodic coastal acidification events. Furthermore, recent laboratory OA experiments reveal that surfclams have a higher tolerance to more acidic waters (0.57  $\Omega_{\text{arag}}$ , Pousse et al., 2020; 1.09  $\Omega_{\text{arag}}$ , Meseck et al., 2021) yet may suffer increased energy expenditure and metabolic losses from the acidic stress (Pousse et al., 2020). This signifies the importance of understanding the carbonate systems when designing future laboratory OA perturbation experiments for different species based on the naturally occurring variation already present within these environments.

## 5 CONCLUSIONS

The MAB and other coastal zones have various biological, chemical, and physical processes that impact acidity and carbonate chemistry. Acidification in coastal zones is further complicated by the influence of these processes varying temporally and spatially. In the winter 2021 survey described here, slope waters of the MAB were strongly influenced by the warm saline Gulf Stream transporting water with a high buffering capacity (high TA) northward. Nearshore and shelf waters were more influenced by terrestrial freshwater inputs and the cold, fresher Labrador Current, leading to higher chlorophyll and oxygen concentrations. Opposing patterns in pH and  $\Omega_{\text{arag}}$  were reflected in both glider datasets, indicating pH and  $\Omega_{\text{arag}}$  were influenced by different drivers. The results described above indicate that pH was more biologically driven while  $\Omega_{\text{arag}}$  was more thermodynamically and chemically driven. Short-term biological and physical events in-

fluenced spatial differences in carbonate parameters over the course of deployment. Understanding and monitoring these short-term seasonal variations in pH and  $\Omega_{\text{arag}}$  is significant for developing experimental designs for understanding and predicting biological responses to acidification based on naturally occurring fluctuations in acidity as well as projected future acidification. Moving forward, the winter deployments analyzed here will contribute to a broader project that will deploy pH gliders in the same region seasonally for the next two years. The integration of my results with those from future missions will allow for a better understanding of the variability and drivers of carbonate chemistry over both space and time in this dynamic, economically important region ■

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