SETTING A BASELINE: INTERANNUAL VARIABILITY OF CARBONATE PARAMETERS IN THE WESTERN SOUTH PACIFIC

By

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ABSTRACT

Surface water samples collected in the western South Pacific Ocean in the austral fall of 2015, 2016, 2017, and 2018, and were used to characterize the variability of carbonate parameters in the region. The main goals of the study were to: 1) Identify if there was significant spatial variability of calcite and aragonite saturation state between temperature-defined sub-regions, and, 2) Identify the magnitudes of and mechanisms behind inter-annual changes in calcite and aragonite saturation state within each sub-region over the 2015-2018 period. The carbonate parameters within the South Pacific Subtropical Gyre remained relatively constant from 2015 through 2018. The Chatham Rise and Subtropical Front region to the east of New Zealand experienced slight increases in temperature and pH over the study period. Between 2015 and 2016, and between 2017 and 2018, there were significant decreases in total alkalinity (TA), while between 2016 and 2017, TA increased. Calcite and aragonite saturation state increased over the four-year study period. Based on sensitivity test results, changes in pH and TA impacted calcite and aragonite state most significantly. To accommodate the opposite sense of change in pH and TA, I hypothesize that there was a large amount of nitrate-supported photosynthesis by calcifying phytoplankton in 2015-2016 and in 2017-2018, specifically, by the coccolith, *E. Huxleyi*, a species prolific in this region, and that in the 2016-2017 period, there may have been nitrate-supported photosynthesis by non-calcifying phytoplankton driving the increase in both pH and TA.
The members of the Defense Committee approve the thesis of Emily Dailey defended on April 17, 2019

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1.0 INTRODUCTION

Due to anthropogenic fossil fuel combustion, cement manufacturing, and land-use change, the partial pressure of carbon dioxide ($pCO_2$) in the atmosphere has increased since the industrial revolution, with the global ocean absorbing a significant fraction (~40%) of the anthropogenic carbon emitted to the atmosphere (Sabine et al., 2004; Salisbury et al., 2008). The global impacts of increasing atmospheric $CO_2$ concentrations on the marine environment are broadly described as “ocean acidification” (OA), and includes a global decrease in oceanic pH and carbonate ion ($CO_3^{2-}$) concentrations (Orr et al., 2005; Takahashi et al., 2014) because when atmospheric $CO_2$ enters the ocean, it undergoes the following reactions:

\[
\begin{align*}
CO_2(g) &\rightarrow CO_2(aq) \quad \text{(Eqn. 1)} \\
CO_2(aq) + H_2O &\rightarrow H_2CO_3 \quad \text{(Eqn. 2)} \\
H_2CO_3 &\rightarrow HCO_3^- + H^+ \quad \text{(Eqn. 3)} \\
HCO_3^- &\rightarrow CO_3^{2-} + H^+ \quad \text{(Eqn. 4)} \\
\end{align*}
\]

(Doney et al., 2009).

As $CO_2(g)$ equilibrates with the surface ocean, it dissolves as $CO_2(aq)$ (Eqn. 1), and subsequently becomes hydrated to form carbonic acid ($H_2CO_3$; Eqn. 2). Since $H_2CO_3$ is unstable at the modern ocean pH, it disassociates in two steps. First, $H_2CO_3$ loses one proton ($H^+$) and produces the bicarbonate ion ($HCO_3^-$; Eqn. 3), which then dissociates again to form $CO_3^{2-}$ and $H^+$ (Eqn. 4). The extent to which the $H_2CO_3$ disassociates is entirely pH dependent; at the current global average pH of 8.1, the relative abundance of $H_2CO_3$, $HCO_3^-$ and $CO_3^{2-}$ is <1%, 90%, and 9%, respectively (Doney et al., 2009). However, as atmospheric $CO_2$ concentrations increase, the continued addition of $CO_2(g)$ to the ocean lowers the pH and consequently the $CO_3^{2-}$ ion...
concentration, as well (Doney et al., 2009). The decrease in CO$_3^{2-}$ ion concentration also affects the ability of seawater to resist a change in pH, also known as its total alkalinity (TA; Stumm & Morgan, 2013), where TA is defined as:

$$\text{TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{SiO(OH)}_3^-] - [\text{H}] - [\text{HSO}_4^-] - [\text{HF}^-] - [\text{H}_3\text{PO}_4] \quad \text{(Eqn. 5)}$$

(Pierrot et al., 2006; Dickson et al., 1981)

In the ocean TA is reasonably approximated by “carbonate alkalinity,” defined as:

$$\text{Carbonate Alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad \text{(Eqn. 6)}$$

Thus, CO$_3^{2-}$ and HCO$_3^-$ are the ocean’s primary “buffers” to changes in pH, including due to OA, although importantly their capacity to resist changes in ocean pH as atmospheric CO$_2$ concentrations increase is limited and decreasing (Feely et al., 2004; Beaufort et al., 2011; Bednarsek et al., 2017).

The impacts of OA on marine life are numerous and well-described, including posing particular challenges for organisms that precipitate calcium carbonate (CaCO$_3$) and consequently rely on adequate concentrations of CO$_3^{2-}$ to live, including coral reefs, shellfish, and phytoplankton such as coccolithophores. Between 14° and 50°S the ocean is a net “sink” of CO$_2$ (Takahashi et al., 2008), meaning atmospheric CO$_2$ is taken up by the ocean’s biological and solubility pumps, lowering atmospheric CO$_2$ concentrations. However, oceanic absorption of atmospheric CO$_2$ leaves the region susceptible to OA impacts, including lowered pH and CO$_3^{2-}$.
concentrations as well as their attendant effects on the biological processes in the region (Sabine et al., 2004; Feely et al., 2004).

In this paper, the biologically important calcium carbonate minerals, calcite and aragonite, are analyzed for the thermodynamic probability of their precipitation, otherwise known as calcite and aragonite saturation state ($\Omega_{\text{cal}}$ and $\Omega_{\text{arag}}$), where:

$$\Omega = \frac{[Ca^{2+}] [CO_3^{2-}]}{K_{sp}}$$  \hspace{1cm} (Eqn. 7)

and where $K_{sp}$ depends on temperature, salinity, pressure, and is specific for the mineral of interest, calcite or aragonite (Doney et al., 2009). Calcite is the more stable of the two minerals and is precipitated by coccolithophores, which are phytoplankton important to the soft-tissue carbon pumps, and foraminifera, which are protzoa (Law et al., 2018). Aragonite, which is more inclined to dissolve in colder waters and/or at higher pressures than calcite, is precipitated by pteropods, trophically-important pelagic snails, and corals, which are important ecosystem builders (Law et al., 2018), especially in the warm shallow waters of the tropical and subtropical ocean. Because calcite is more stable than aragonite, $\Omega_{\text{cal}}$ will always be higher than $\Omega_{\text{arag}}$, and aragonite-forming organisms are more susceptible to dissolution due to undersaturation, defined as $\Omega < 1$ (Orr et al., 2005) because waters will become undersaturated with respect to aragonite before they will with respect to calcite. Due to the relatively high and invariant concentrations of the calcium ion ($Ca^{2+}$) in the ocean, spatial and temporal variability in $\Omega$ in the surface ocean is primarily due to variability in the $CO_3^{2-}$ ion concentration. As the ocean acidifies due increasing
atmospheric CO$_2$ concentrations, CO$_3^{2-}$ ion concentrations will decrease, lowering $\Omega$ and putting calcifying organisms at increasing risk (Orr et al., 2005).

Globally, the carbonate system is impacted by increasing atmospheric CO$_2$ concentrations (Feely et al., 2004; Doney et al., 2009; Jiang et al., 2015), but the carbonate system can also be significantly perturbed by other mechanisms on shorter timescales (Fujii et al., 2009; Kuchinke et al., 2014). In the western South Pacific, mechanisms such as seasonal trends in primary productivity, increased air-sea gas exchange due to changes in wind strength, and El Nino/Southern Oscillation (“ENSO”) events all impact the regional carbon cycle (Fujii et al. 2009). Fujii et al. (2009) explicitly states that the region is relatively understudied with respect to long-term monitoring of inter-annual and decadal variability; the paper highlights the need to collect and analyze more data in the subtropical Pacific. Monitoring and analyzing short-term, inter-annual changes in carbonate parameters is necessary to quantify and contextualize long-term OA trends (Fujii et al. 2009). The purpose of this paper is to quantify changes in calcite and aragonite saturation state over a four-year period in order to understand the magnitude of change that can be expected on inter-annual timescales and to explore the relative importance of mechanisms that might be driving these inter-annual changes.

2. METHODS

2.1 Data Sources

Samples were collected aboard the SSV Robert C. Seamans, a research-outfitted tall ship owned and operated by Sea Education Association (SEA; www.sea.edu). Each cruise began the last week in March and ended the first week in May during the austral fall of 2015, 2016, 2017, and 2018. All cruises in this study crossed from Christchurch, New Zealand to Pape’ete, Tahiti, in French Polynesia (Fig. 1A. Additionally, a composite carbon system parameter dataset from the
GLODAP, CARINA, and LDEO databases was used to compare pH, TA, Ω\text{cal} and Ω\text{arag} from this study with those from 2005 (Takahashi et al., 2014; Fig. 2).

Figure 1. Map of four cruises from which the samples used in this study originated. All samples were collected from aboard the SSV Robert C. Seamans on transects from Christchurch, New Zealand to Pape’ete, French Polynesia (A). Map of the sea surface temperature for the study area in austral fall, with contours at 18°C, 22°C, and 25°C (B). The region between 174°E and 174°W, and between 42.5°S and 44.8°S, with bathymetry <2000 m is defined as the CR. The CR/STF are defined as the region in blue, with <18°C SST. The SPSG is defined as the region with >18°C SST, and is further subdivided into the SSPSG (18°C to 22°C), the CSPSG (22°C to 25°C) and the NSPSG (>25°C).
Figure 2. Map of all data points (black dots) from the Takahashi et al. (2014) dataset, with carbonate values from the year 2005. White contours separate water masses at defined in Fig. 2b. Data south of the 14°C contour was defined as SAW, and was not used in this study.

2.2 Regional Oceanography

Globally, the subtropical front (STF) is a band that separates colder, fresher, sub-Antarctic waters (SAW) from the warmer, saltier, subtropical waters (STW) of all major oceans (Hadfield et al., 2007). However, the shallow bathymetry of the submerged continent of Zealandia interacts with the STF in this region (Fig. 3; Chiswell et al., 2015). To the south, the STF is bent around the south coast of the South Island of New Zealand while colder, deeper SAW is uplifted over the Campbell Plateau (Fig. 3; Chiswell et al., 2015). This cold water continues north along the east coast of the South Island in a current called the Southland Current (SC; Fig. 3; Longhurst, 2007; Chiswell et al., 2015). New Zealand’s North Island also intersects a zonal current; at 33-35°S, the Tasman Front (TF), a warm, salty current, runs along the north side of the Tasman Sea (Fig. 3; Chiswell et al., 2015). Its characteristically warm water is forced north around the west side of the North Island of New Zealand, and turns south down the east coast of the North Island (Fig. 3; Chiswell et al., 2015)
On the eastern side of New Zealand, the two currents, the warm continuation of the southward-flowing TF and the northward-flowing SC, meet and continue eastward over another bathymetric feature, the Chatham Rise (CR; Fig.3; Chiswell et al., 2015). The CR continues for about 800 km east of the South Island, over which a portion of the STF is “locked” to the relatively shallow bathymetry (Fig. 3; Hadfield et al., 2007). At about 174° W, the submerged continent ends and the STF continues unconstrained by CR bathymetry; for the purposes of this study, this bathymetrically-unconstrained region is denoted as the “STF” (Fig 3. Chiswell et al., 2015).
Figure 3. This map highlights the major water masses, bathymetry, fronts, and currents influencing samples examined in this study. The warm Tasman Front (TF) is indicated by red arrows while the cold Southland Current (SC) and uplifted cold waters from the south are indicated by blue arrows. The two mix to the east of New Zealand and are indicated by purple arrows continuing eastward to the dynamic mixing regions of the Chatham Rise (CR) and Subtropical Front (STF).

The STF, including its CR subcomponent, is a frontal mixing zone between STW to the north and SAW to the south, characterized by a strong SST gradient (Fig. 3; Graham & De Boer, 2013). Therefore, the CR and STF are physically defined as the area between the STW (SST>18°C, SSS>35.1 psu) and the SAW (SST<14°C, SSS<34.6 psu; Sutton, 2001; Figs. 2b and 3). For the purposes of this study, SST was the primary metric used to delineate the boundaries
of the CR/STF region (Figs. 1B and 2), although in addition to temperature, the STW and SAW have different micro and macro nutrient distributions. Specifically, the CR/STF represents a mixing region between the relatively Fe-rich but macro-nutrient (i.e., nitrate and phosphate) poor STW of the South Pacific Subtropical Gyre (SPSG) and the Fe-poor, macro-nutrient-rich SAW, leading to elevated primary productivity compared to its neighboring water masses (Hadfield et al., 2007; Chiswell et al., 2013).

North of the CR/STF region the SPSG has water mass characteristics of STW – warmer (>15°C) and saltier than that of the CR region (Sutton, 2001; Chiswell et al., 2015). Since these cruises were in early fall, SST was still relatively elevated compared to the annual mean, and so SPSG was defined as any region with surface waters >18°C. Additionally, a large range of SSTs was observed within the SPSG (18°C to 29°C). Because SST has a large impact on carbonate equilibria and saturation state (Salisbury & Jönsson, 2018), the SPSG was further split into three temperature bins: the Southern South Pacific Subtropical Gyre (SSPSG) with SSTs between 18º to 22ºC, the Central South Pacific Subtropical Gyre (CSPSG) with SSTs between 22ºC to 25ºC, and the Northern South Pacific Subtropical Gyre (NSPSG) with SSTs >25ºC (Figs. 2B and 3). Carbonate parameters were evaluated within each temperature-defined water mass. The number of samples from each sub-region is outlined in Table 1.
The number of samples used to find average values of carbonate parameters from each SST-defined sub-region.

<table>
<thead>
<tr>
<th>Year</th>
<th>CR</th>
<th>STF</th>
<th>SSPSG</th>
<th>NSPSG</th>
<th>CSPSG</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005</td>
<td>2</td>
<td>15</td>
<td>16</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>2015</td>
<td>11</td>
<td>16</td>
<td>7</td>
<td>3</td>
<td>12</td>
</tr>
<tr>
<td>2016</td>
<td>2</td>
<td>8</td>
<td>8</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>2017</td>
<td>3</td>
<td>8</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>2018</td>
<td>8</td>
<td>0</td>
<td>16</td>
<td>14</td>
<td>4</td>
</tr>
<tr>
<td>Total</td>
<td>26</td>
<td>47</td>
<td>51</td>
<td>59</td>
<td>34</td>
</tr>
</tbody>
</table>

Table 1. The number of samples used to find average values of carbonate parameters from each SST-defined sub-region.

2.3 Data Collection

Surface samples were collected daily for pH and alkalinity analysis in the shipboard lab. Samples were either collected using a rosette with Niskin bottles or by deploying a bucket over the side. Samples collected from the Niskin rosette (SBE19PlusV2, SeaBird Electronics, Bellevue, WA) were collected at < 3m within the mixed layer (Hadfield et al., 2007). Surface samples collected using a bucket were rinsed three times with surface water before collection and processing. Sea surface temperature and salinity were continuously monitored by the ship’s underway flow-through thermosalinograph (SBE45MicroTSG, SeaBird Electronics, Bellevue, WA) system which sampled from 0 to 2 m depth.

2.4 pH

Samples for pH analysis were transferred from Niskin bottles to 250 mL amber glass bottles. pH was measured using the spectrophotometric method following Clayton & Byrne (1993) and Dickson et al. (2007). Specifically, a 10-cm pathlength glass cuvette was triple-rinsed with a dilute HCl solution, triple-rinsed with deionized (DI) water, and dried. The cuvette was filled with sample and its absorbance was measured at three wavelengths: 434, 578, and 730 nm.
Finally, 75 µL of purple m-cresol dye was added to the cuvette and the absorbance of the sample was measured a final time at the same wavelengths.

2.5 Total Alkalinity

Surface seawater samples were collected via Niskin bottles or bucket and transferred to darkened glass bottles, and were processed within six hours of sample collection. Total alkalinity was measured using the Gran Titration Method (Andersen, 2002). First, all instruments, including glassware, the pH probe, and the magnetic stirrer, were triple-rinsed with sample. Then, 100 mL of sample was measured using a volumetric flask, and transferred to a glass jar where it was simultaneously mixed using a magnetic stir-bar and measured for changes in pH. Subsequently, 0.4 mL increments of 5% HCl were added to the sample and the resulting decrease in pH was recorded. Once the pH was <3.3, HCl added was added in 0.05 mL increments until the sample reached a final pH of 2.2. The slope of the curve was used to determine the TA with sharp drops in pH indicating the margins at which the solution had reached buffering capacity.

3. RESULTS

3.1 Calculating Carbonate Parameters using CO2_sys

Shipboard measurements from the four cruises were used to calculate additional carbonate system parameters using CO2_sys for Excel (Pierrot & Wallace, 2006). In CO2_sys, input parameters included lab temperature, pressure, and salinity of the water sampled, while output parameters included the depth at which the sample was collected and the \textit{in situ} temperature. The dissociation constants $K_1$ and $K_2$ from Mehrbach et al. (1973), refit by Dickson and Millero (1987), the KHSO$_4$, which is the dissociation constant for HSO$_4^-$, from Dickson (1990), the seawater pH scale, and the total Boron concentration ([B]T) defined by Uppstrom (1974) were used for calculations. Measured pH and TA values were used as input parameters from which
additional carbonate parameters of interest, including *in situ* pH, $\Omega_{\text{arag}}$, and $\Omega_{\text{cal}}$, were calculated. Additionally, carbonate data from the OCADS dataset (Takahashi et al., 2014), including pCO$_2$ and TA data were used as input parameters for CO2_sys and were used to calculate pH, $\Omega_{\text{cal}}$, and $\Omega_{\text{arag}}$ for the reference year 2005. All reported values are means ± 1 standard deviation.

### 3.2 Spatial Variability of $\Omega_{\text{cal}}$ and $\Omega_{\text{arag}}$ between the CR and STF regions

Carbonate parameters within the CR/STF varied more over interannual timescales than carbonate parameters in the gyre did. Comparing the CR and STF indicates that $\Omega_{\text{cal}}$ and $\Omega_{\text{arag}}$ distributions between the two regions were not significantly different when averaged over the 2015 to 2017 period. (Figs. 4a and 4e; Table 2). In the CR, mean $\Omega_{\text{cal}}$ was 4.28 ± 0.55, while in the STF, mean $\Omega_{\text{cal}}$ was 4.21 ± 0.60. Data was not collected in the STF in 2018, but when 2018 data from the CR is also considered, a statistically significant difference between the regions appeared, with mean $\Omega_{\text{cal}}$ of 4.67 ± 0.51 in the CR and 4.21 ± 0.60 in the STF (2-tailed unpaired t-test assuming unequal variances, $p = 0.009$, $a = 0.05$; Figs. 4c and 4e; Table 2). For distributions of $\Omega_{\text{arag}}$, the same trend held true; the 2015 to 2017 period showed no significant difference between the water masses with a mean CR $\Omega_{\text{arag}}$ of 2.87 ± 0.26 and a mean STF value of 2.72 ± 0.39 (Figs. 4b and 4f) while the $\Omega_{\text{arag}}$ in the STF in the 2015–2018 period was 2.77 ± 0.35, significantly lower than the $\Omega_{\text{arag}}$ in the CR, 2.86 ± 0.46 (2-tailed unpaired t-test assuming unequal variances, $p = .009$, $a = 0.05$; Figs. 4d and 4f; Table 2).

<table>
<thead>
<tr>
<th></th>
<th>2015-2017</th>
<th>2015-2018</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Omega_{\text{cal}}$</td>
<td>$\Omega_{\text{arag}}$</td>
</tr>
<tr>
<td>CR/STF</td>
<td>4.28 ± 0.35</td>
<td>2.77 ± 0.35</td>
</tr>
<tr>
<td>SSPSG</td>
<td>4.88 ± 0.50</td>
<td>3.17 ± 0.32</td>
</tr>
<tr>
<td>CSPSG</td>
<td>5.41 ± 0.60</td>
<td>3.55 ± 0.40</td>
</tr>
<tr>
<td>NSPSG</td>
<td>5.92 ± 0.49</td>
<td>3.93 ± 0.34</td>
</tr>
</tbody>
</table>

Table 2. Mean ± 1 S.D. $\Omega_{\text{cal}}$ and $\Omega_{\text{arag}}$ for 2015-2017 (left) and 2015-2018 (right) for the CR/STF, SSPSG, CSPSG, and NSPSG.
Figure 4. Distributions of $\Omega_{\text{cal}}$ (A and C) and $\Omega_{\text{arag}}$ (B and D) for samples collected in 2015 (circles), 2016 (squares), and 2017 (diamonds; A and B) or 2015 through 2018 (triangles), and when the 2018 CR data is included (C and D). Data was not collected from the non-CR STF in 2018. Mean ± 1 S.D. $\Omega_{\text{cal}}$ for 2015 through 2017 (left) and 2015 through 2018 (right) data, evaluated for the CR (light blue bars) and STF (dark blue bars; E). Mean ± 1 S.D. $\Omega_{\text{arag}}$ for 2015 through 2017 (left) and 2015 through 2018 (right) data, evaluated for the CR (light blue bars) and STF (dark blue bars; F).
3.3 Spatial Variability within the SPSG

Within the SPSG, there was statistically significant spatial variability in Ω(cal) between the CSPSG and the NSPSG, with mean values of 5.73 ± 0.69 and 6.69 ± 0.97, respectively, as well as between the CSPSG and the SSPSG with mean values of 5.73 ± 0.69 and 5.10 ± 0.44, respectively, but not between the SSPSG and the NSPSG, which had the largest difference in means of 6.69 ± 0.97 and 5.10 ± 0.44, respectively (Fig. 6; 2-tailed unpaired t-test assuming unequal variance, p = 0.0007, p = 0.0001, p = 7.91, a = 0.05). Distributions of Ω(arag) (Fig. 5A) show less spatial variability than Ω(cal) (Fig. 5B), with significant differences in mean Ω(arag) between the CSPSG (3.76 ± 0.46) and the NSPSG (4.45 ± 0.65; Fig. 6; 2-tailed unpaired t-test assuming unequal variances, p = .0003, a = 0.05), but not between the CSPSG and the SSPSG, which had a mean Ω(arag) value of 3.31 ± 0.29.

Figure 5. Distributions of Ω(cal) (A) and Ω(arag) (B) with temperature boundaries as in Fig. 2B and symbols as per Fig. 4.
Figure 6. Mean (± 1 S.D.) $\Omega_{\text{cal}}$ (dark blue) and $\Omega_{\text{arag}}$ (light blue) in sub-regions of the SPSG.

3.4 Inter-annual Variability in SST

Given the role of sea surface temperature (SST) in affecting $\Omega$, I considered whether SST changed significantly over the study period. SST did not significantly change within the SPSG over the four-year period; the mean SST of the region was $22.8 \pm 2.3^\circ C$ and varied by $<1^\circ C$ each year. However, two sub-regions of the SPSG did change significantly between 2015 and 2018. The SST of the NSPSG increased significantly between 2015 ($25.8 \pm 0.9^\circ C$) and 2018 ($27.9 \pm 1.2^\circ C$; Fig. 7; 2-tailed unpaired t-test assuming unequal variances, $p=0.02$, $a=0.05$). However, the NSPSG did not change significantly between 2005 and 2018, with a mean SST of $27.9 \pm 1.5^\circ C$ in 2005 and $27.9 \pm 1.2^\circ C$ in 2018 (Fig. 7; 2-tailed unpaired t-test assuming unequal variances, $a=0.05$), suggesting that perhaps 2015 was a year with anomalously low SST. Additionally, the mean NSPSG SST of $27.5 \pm 1.3^\circ C$ in 2015-2018 was not statistically different than the 2005 value, $27.9 \pm 1.5^\circ C$ (Figs. 7 and 8; 2-tailed t-test assuming unequal variances, $a=0.05$). In the SSPSG a statistically significant SST decrease occurred between 2015 ($20.0 \pm 0.9$
°C) and 2018 (19.0 ± 0.4°C; Fig. 7; 2-tailed unpaired t-test assuming unequal variances, p=0.03, a=0.05). The SSPSG showed trends opposite those of the NSPSG in that the 2005 mean value of 20.2 ± 1.2 °C is significantly higher than the 2018 mean SST of 19.0 ± 0.4 °C, but is not statistically different from the 2015 mean SST of 20.0 ± 0.9 °C (Fig. 7). This suggests that 2018 was a relatively cool year for SST in the SSPSG. Alternatively, the cruise in 2018 may have sampled different/deeper water masses, as a tropical storm impacted the sampling region, potentially introducing deeper/cooler water masses into surface waters. In the SPSG as a whole, the mean SST did not change significantly between the 2005 (25.3 ± 3.6°C) and the 2015-2018 period (22.8 ± 3.3°C; Fig. 8; 2-tailed t-test assuming unequal variances, a=0.05).

The SST of the CR/STF region was significantly higher during the 2015-2018 period (16.2 ± 0.8°C) than it was in 2005 (15.2 ± 1.7°C; Figs. 7 and 8; 2-tailed unpaired t-test assuming unequal variances, p = 0.03, a = 0.05). However, within the 2015 to 2018 period, there are no statistically significant differences between mean SST’s of adjacent years based on 2-tailed unpaired t-tests assuming unequal variances with alpha values of 0.05. However, when averaged together, 2015 and 2016 had a lower mean SST (16.1 ± 0.8°C) than 2017 and 2018 (16.6 ± 0.8°C; 2-tailed unpaired t-test assuming unequal variances, p=0.01, a=0.05).
Figure 7. Mean (±1 S.D.) SST for each of the regions in each of the study years. Note that April 2005 is shown for comparison with samples collected from 2015 through 2018.

Figure 8. Distributions of SST from 2005 OCADS data (Takahashi et al., 2014; A) and the mean data from 2015 through 2018 sampling (B)
### 3.5 Interannual Variability of pH

Between 2015 and 2018 the increase in pH in the CR from (7.99 ± 0.05) to (8.17 ± 0.03) is not significant, nor is the increase in pH in the STF between 2015 (7.98 ± 0.07) and 2017 (8.12 ± 0.04; 2-tailed unpaired t-test assuming unequal variances and an alpha-value of 0.05). In the CR/STF combined region, the increase in pH between 2015 (7.98 ± 0.06) and 2018 (8.17 ± 0.03) is also not significant (2-tailed unpaired t-test assuming unequal variances and an alpha-value of 0.05). Between 2005 and the 2015 to 2018 period, the mean pH in the CR/STF combined region decreased from 8.10 ± 0.01 to 8.05 ± 0.09 (Figs. 9 and 10; 2-tailed t-test, p = .0008, a = 0.05). Between 1999 and 2003, the SAW of the Munida time series off the east coast of NZ, to the south of the CR/STF, showed an actual variability in pH of only about 0.6, but models for the same time period showed interannual variability of up to 0.9 (Law et al., 2018). This magnitude of variability allows for the observed 0.05-unit decrease in pH in the CR/STF region from 2005 to the 2015-2018 period. However, the large fluctuations in pH within the 2015-2018 period cannot be supported by even the largest pH changes observed in the Law et al. (2018) study.

In the SPSG, there is no significant variability of pH within the 2015 (8.03 ± 0.02) to 2018 period (8.14 ± 0.08) or from 2005 (8.09 ± 0.01) to the 2015 to 2018 period (8.10 ± 0.08; 2-tailed unpaired t-test assuming unequal variances; Figs. 9 and 10). The SPSG also experienced an increase in pH, but of a smaller magnitude; the SPSG had a mean pH of 8.03 ± 0.02 in 2015, which only increased to 8.14 ± 0.08 in 2018 (Fig. 9), however, based on a 2-tailed unpaired t-test assuming unequal variances and an alpha-value of 0.05, the mean pH value between the 2015 and 2018 were not statistically different means. This 0.11-unit change was still relatively large compared to observed maximum interannual pH changes in the northeast Atlantic subtropical gyre - a comparable ocean region which exhibited variability of only <0.05 (Casiano et al.,
Although the SPSG was more variable with regard to pH than expected, it was still less variable than the CR/STF. This reflects the greater seasonality in temperature, physical mixing, and biological productivity of the CR/STF sub-region, all of which impact the carbonate system (Law et al., 2018).

**Figure 9.** Mean (±1 S.D.) pH from each water mass and temperature bin is plotted for each year of the study. There is variability in the data, but there is not a statistically significant difference between 2015 and 2018.

**Figure 10.** Distribution of surface ocean pH for April 2005 (Takahashi et al., 2014) (a) compared with the distribution of surface ocean pH 2015-2018 period (b).
3.6 Interannual Variability of TA

In the CR/STF, the mean TA decreased significantly within the 2015 to 2018 period from $2.5 \pm 0.2$ meq/L in 2015 to $2.3 \pm 0.1$ meq/L in 2018 (Fig. 11; 2-tailed t-test assuming unequal variances, $p = 0.002$, $a = 0.05$). However, when 2015 and 2016 are averaged together and 2017 and 2018 are averaged together, the decrease over the 2015 to 2018 period was not statistically significant (2-tailed unpaired t-test assuming unequal variances, $a=0.05$). Additionally, some years within the range showed inter-annual variability. The mean TA in 2015 was $2.5 \pm 0.2$ meq/L and was significantly higher than mean TA in 2016, $2.3 \pm 0.1$ meq/L (Fig. 11; 2-tailed t-test assuming unequal variances, $p=0.002$, $a=0.05$). The mean TA in 2017, $2.4 \pm 0.1$ meq/L was significantly higher than the mean TA in 2018, $2.3 \pm 0.1$ meq/L (Fig. 11; 2-tailed t-test assuming unequal variances, $p=0.03$, $a=0.05$). In contrast to the overall decrease in TA in the CR/STF over the 2015-2018 period, TA slightly increased from 2005 to the 2015-2018 period from $2.3 \pm 0.01$ meq/L to $2.4 \pm 0.2$ meq/L (Fig. 12; 2-tailed t-test assuming unequal variances, $p = 0.02$, $a = 0.05$). The overall increase in TA in the CR/STF between 2005 and the 2015 period is opposite the decreasing trend within the 2015 to 2018 period (Figs. 11 and 12).

In the SPSG, mean TA values do not change significantly between 2015 and 2018 according to a 2-tailed t-test assuming unequal variances and an alpha-value of 0.05 (Fig. 11). However, when 2015 and 2016 are averaged together and 2017 and 2018 data are averaged together, there is a statistically significant decrease in TA from 2015-2016 ($2.5 \pm 0.1$ meq/L) to 2017-2018 ($2.4 \pm 0.1$ meq/L) in the SPSG (Fig. 11; 2-tailed t-test assuming unequal variance, $p = .0004$, $a = 0.05$). The mean TA in 2005 was $2.3 \pm 0.02$ was not significantly different than the mean 2015-2018 period, $2.4 \pm 0.1$ meq/L (Fig. 12; 2-tailed t-test assuming unequal variances, $a=0.05$).
Figure 11. Mean (±1 S.D.) Total alkalinity for the study regions. 2005 data from Takahashi et al. (2014) are compared with samples collected in 2015 through 2018.

Figure 12. Distributions of TA from 2005 (Takahashi et al., 2014; A) and the 2015 to 2018 samples (B).

3.7 Interannual Variability of $\Omega$

With regard to $\Omega$, the CR/STF region appears to be no more or less variable interannually than the SPSG, although certainly is distinguishable from the gyre by it’s universally lower $\Omega_{cal}$.
and Ω_{arag} values. The CR/STF region showed a maximum variability of Ω_{cal} of 27%, while the NSPSG showed 24%, the CSPSG showed 28%, and the SSPSG showed 20% - values very similar to that of the CR/STF region. This was surprising, as Ω is largely dependent on pH, which was more variable in the CR/STF than the SPSG. Overall, the spatial distribution of the magnitude of pH variability throughout the study region concurs with the expectation that the frontal mixing CR/STF region would be more variable with regard to carbonate parameters than the relatively stable, warmer, less productive subtropical gyre.

In the SPSG as a whole, neither appeared Ω_{cal} or Ω_{arag} to change significantly over the 2015 to 2018 period. However, when analyzed individually, all sub-regions of the SPSG showed statistically significant increases in both Ω_{cal} and Ω_{arag} between 2015 and 2018. In the NSPSG, the northernmost bin, Ω_{cal} increased significantly from a mean value of 5.60 ± 0.32 in 2015 to a mean value of 6.96 ± 0.97 in 2018 (Fig. 13A; 2-tailed unpaired t-test assuming unequal variances, p=0.001, α=0.05) and Ω_{arag} increased from 3.71 ± 0.22 in 2015 to 4.63 ± 0.64 in 2018 (Fig. 13B; 2-tailed unpaired t-test assuming unequal variances, p=0.001, α=0.05). In the CSPSG, Ω_{cal} significantly increased from 5.37 ± 0.35 in 2015 to 6.22 ± 0.53 in 2018 (Fig. 13A; 2-tailed unpaired t-test assuming unequal variances, p=0.0001, α=0.05) and Ω_{arag} increased from 3.52 ± 0.05 in 2015 to 4.08 ± 0.35 in 2018 (Fig. 13B; 2-tailed unpaired t-test assuming unequal variances, p=0.0001, α=0.05). In the SSPSG, the southernmost bin, Ω_{cal} increased from 4.76 ± 0.41 in 2015 to 5.26 ± 0.44 in 2018 (Fig. 13A; 2-tailed unpaired t-test assuming unequal variances, p=0.02, α=0.05) and Ω_{arag} increased from 3.10 ± 0.27 in 2015 to 3.41 ± 0.28 in 2018 (Fig. 13B; 2-tailed unpaired t-test assuming unequal variances, p=0.02, α=0.05).

Between 2005 and the 2015-2018 period, Ω_{cal} and Ω_{arag} also increased in all sub-regions of the SPSG. In the NSPSG, Ω_{cal} increased from 5.90 ± 0.16 in 2005 to an average of 6.69 ± 0.97
over the 2015-2018 period (Figs. 13A and 14; 2-tailed unpaired t-test assuming unequal variances, p=0.003, a=0.05) and Ω_{arag} increased from 3.93 ± 0.12 in 2005 to an average value of 4.44 ± 0.65 over the 2015-2018 period (Figs. 13B and 15; 2-tailed unpaired t-test assuming unequal variances, p=0.001, a=0.05). In the CSPSG, Ω_{cal} increased from 5.45 ± 0.14 in 2005 to an average of 5.73 ± 0.69 over the 2015-2018 period (Figs. 13A and 14; 2-tailed unpaired t-test assuming unequal variances, p=0.04, a=0.05) and Ω_{arag} increased from 3.58 ± 0.09 in 2005 to an average value of 3.76 ± 0.46 over the 2015-2018 period (Figs. 13B and 15; 2-tailed unpaired t-test assuming unequal variances, p=0.04, a=0.05). In the SSPSG, Ω_{cal} increased from 4.81 ± 0.25 in 2005 to an average value of 5.10 ± 0.44 in the 2015-2018 period (Figs. 13A and 14; 2-tailed unpaired t-test assuming unequal variances, p=0.01, a=0.05) and Ω_{arag} increased from 3.13 ± 0.18 in 2005 to an average value of 3.31 ± 0.29 over the 2015-2018 period (Figs. 13B and 15; 2-tailed unpaired t-test assuming unequal variances, p=0.02, a=0.05).

**Figure 13.** (A) mean (± 1 S.D.) Ω_{cal} of each of the four water masses/temperature bins of interest, is plotted for each of the five study years. (B) mean (± 1 S.D.) Ω_{arag} of each of the four water masses/temperature bins of interest, is plotted for each of the five study years.
Figure 14. $\Omega_{\text{cal}}$ is gridded over the study region with x:25 and y:25. Panel A shows the 2005 OCADS data, with stations plotted in black dots, while panel B shows SEA cruises from 2015 to 2018.

Figure 15. $\Omega_{\text{arg}}$ is gridded over the study region with x:25 and y:25. Panel A shows the 2005 OCADS data, with stations plotted in black dots, while panel B shows SEA cruises from 2015 to 2018.

4. DISCUSSION

In order to discern the drivers of the observed changes in $\Omega$ both interannually and spatially, it was necessary to first determine which CO2_sys input parameters (SST, pH, or TA) were primarily increasing $\Omega$. Therefore, I ran sensitivity tests to identify which parameters contributed
most to observed changes in $\Omega_{\text{cal}}$ and $\Omega_{\text{arag}}$. I did this by taking the 2015 data for SST, SSS, TA, pH, and lab temperature and inputting all values into CO2_sys for both the CR/STF and the SPSG regions. Then, I changed the variables one at a time to see which were largely driving the observed changes in $\Omega_{\text{cal}}$ and $\Omega_{\text{arag}}$. For each parameter of interest, I inputted the 2015 mean value of that variable, then did the same for the 2018 value. By calculating the $\Omega_{\text{cal}}$ and $\Omega_{\text{arag}}$ using the mean values from these years, I was able to identify how much the observed changes in input parameters impacted the $\Omega_{\text{cal}}$ and $\Omega_{\text{arag}}$. This was necessary because in order to propose mechanisms for the observed interannual increases in both $\Omega_{\text{cal}}$ and $\Omega_{\text{arag}}$, it was necessary to analyze which carbonate parameters were largely driving changes in the region.

Within the SPSG region as a whole, as well as in each of its sub-regions, $\Omega_{\text{cal}}$ and $\Omega_{\text{arag}}$ showed overall increasing trends over the 2015 to 2018 period. In the SPSG as a whole, $\Omega_{\text{cal}}$ increased by .89, or 17%, in the NSPSG, $\Omega_{\text{cal}}$ increased by 24%, in the CSPSG $\Omega_{\text{cal}}$ increased by 16%, and in the SSPSG, $\Omega_{\text{cal}}$ increased by 10.5% (Fig. 13). Sensitivity tests indicated that the observed changes in SST of $\pm$ 2°C, change $\Omega_{\text{cal}}$ and $\Omega_{\text{arag}}$ only by 1-2%. This suggests that interannual mechanisms that perturbed SST alone were not responsible for the observed increase in $\Omega_{\text{cal}}$ or $\Omega_{\text{arag}}$. The mean decrease in TA in the SPSG from the mean 2015-2016 value of 2.49 $\pm$ 0.13 meq/L to the mean 2017-2018 value of 2.37 $\pm$ 0.12 meq/L, coincides with a 4.5% decrease in both $\Omega_{\text{cal}}$ and $\Omega_{\text{arag}}$ – opposite the observed trend, although not of a particularly large magnitude, especially compared to the overall observed increase of 17%. The observed change in pH from 8.03$\pm$0.02 in 2015 to 8.14$\pm$0.08 from 2015 to 2018, would account for a 22% increase in $\Omega_{\text{cal}}$ and $\Omega_{\text{arag}}$. This change in pH was not statistically significant, but is the only input parameter with a relative impact on $\Omega_{\text{cal}}$ and $\Omega_{\text{arag}}$ large enough to cause the observed increases.
The relative importance of each of these carbonate parameters in influencing $\Omega$, and the direction which they perturbed $\Omega$, could not be explained by any of the usual mechanisms of the region. El Niño and La Niña events certainly have impacts on the SPSG; El Niño conditions produce cooler SSTs while La Niña conditions produce warmer SST’s (Linsley et al., 2000). However, based on the above sensitivity tests, it became clear that changes in SST were not driving the observed changes in $\Omega_{\text{cal}}$ and $\Omega_{\text{arag}}$. 2015 and 2016 were El Niño years, which should have been reflected by lower SST in the gyre, while 2017 and 2018 were weak La Niña years, which should have been reflected by higher SST in the gyre. However, only in the northernmost part of the gyre, did SST increase significantly, from 25.8±0.85°C in 2015 to 27.9±1.24°C in 2018 (Fig. 7; 2-tailed unpaired t-test assuming unequal variances, $p=0.02$, $a=0.05$). The increase in SST demonstrated in this region may partially explain why this sub-region of the SPSG demonstrated the greatest increase in $\Omega_{\text{cal}}$ and $\Omega_{\text{arag}}$. However, the relative importance of variability of SST remains very low when implicating drivers for observed changes in $\Omega$, and the observed increases in $\Omega$ must largely be derived from perturbations in other input variables ($pH$ and TA).

The SPSG has highest productivity rates in the spring (Longhurst, 2007), and these cruises sampled in austral fall (April). Therefore, primary production of either calcifying or non-calcifying organisms is unlikely to be the driver of interannual changes in the SPSG, as it would have likely been several months since a bloom, and any signatures of such a bloom in the surface ocean would have likely been since removed. Ocean acidification (OA) likely would not be detected on this short of a timescale, but even so, the region does not show the chemical signature of OA; OA is defined by decreasing $pH$, TA, and $\Omega$ with respect to time (Doney et al., 2009). TA does decrease over this time period, but both $pH$ and $\Omega$ increase, which suggests that
TA was perturbed by a precipitation event of CO$_3^{2-}$ or HCO$_3^-$, rather than by acidification of the system. The trends of carbonate parameters in the SPSG do not highlight one likely mechanism.

A next step for a future study in elucidating the processes that left these puzzling chemical signatures in the SPSG, is to obtain chlorophyll-a (chl-a) and particulate inorganic carbon (PIC) data for the SPSG from February, April, and May of 2015, 2016, 2017, and 2018. Chl-a data would show the amount of primary productivity occurring in surface waters while PIC data would show if there were large areas where calcifying phytoplankton, such as coccolithophores, had bloomed. This data is accessible via satellite images from the Moderate Resolution Imaging Spectroradiometer (MODIS), where monthly distributions of chl-a and PIC are plotted and made available. The SPSG lies outside of the “global calcite belt” (discussed below; Balch et al., 2011), but due to the overall decreases in TA with concurrent increases in pH, it is important to identify if calcifying blooms, such as those of coccolithophores, were happening in the SPSG. These blooms can occur in subtropical gyres (Tyrell & Merico, 2004), but are much more likely to occur between 30˚S and 60˚S (Balch et al., 2011).

In the CR/STF region between 2015 and 2018, $\Omega_{\text{cal}}$ increased by 0.9 or 21%, an incredibly large change, considering that in the Gulf of Maine, a region warming more rapidly that 99% of the global ocean, $\Omega_{\text{arag}}$ only increased by ~9.0% during four years of its most dramatic change (Salisbury & Jönsson, 2018). Over the 2015-2018 period in the CR/STF region, SST increased by .2°C and salinity did not change at all; the combined impact of the observed changes SST and SSS implicated a maximum $\Omega_{\text{cal}}$ increase of <1%. Assuming that the 0.2 increase in pH between 2015 and 2018 in the CR/STF actually occurred, despite the lack of statistical significance, $\Omega_{\text{cal}}$ would have increased by 42-52% from the 2015 values. This change alone far exceeds the observed increase in $\Omega_{\text{cal}}$ of 21%. However, TA decreased between 2015
and 2018 by \(-0.25\) meq/L. A decrease of this magnitude would drive a decrease in \(\Omega_{\text{cal}}\) of 10-11\%. Altogether, these changes in input parameters implicated an increase in \(\Omega_{\text{cal}}\) of the region by 56-67\%, which is far greater than the 21\% observed. However, the 0.2 increase in pH between the two years was not found to be statistically significant based on a 2-tailed t-test assuming unequal variances.

Assuming that the relative change of SST, SSS, and TA and their impacts on \(\Omega_{\text{cal}}\) were accurate, an increase in pH of about .1 between 2015 and 2018 would be required to raise \(\Omega_{\text{cal}}\) by the observed 21\%. Although this relative contribution of pH change is only half that of the observed change in pH, the observed change was not found to be statistically significant. Therefore, assuming a lower magnitude of change in pH in order to fit the statistically significant change in \(\Omega_{\text{cal}}\) seems like the most appropriate interim step to implicating possible driving mechanisms of strong interannual variability of \(\Omega_{\text{cal}}\) in the CR/STF. The mechanisms explained henceforth assume the following estimated relative contributions of the input parameters to the 2015-2018 increase in \(\Omega_{\text{cal}}\) in CR/STF: SST & SSS: <1\%, TA: -11\% to -12\%, and pH: 16\% to 23\%.

As stated earlier, El Niño and La Niña are large sources of climatic interannual variability, and have large impacts on SST (Shaw et al., 1999; Hopkins et al., 2010). During El Niño events, SST in the STF and in STW east of New Zealand cool (Shaw et al., 1999; Hopkins et al., 2010). From 1990 to 1992, an El Niño occurred, and the SST of the STW, like that of the SPSG, cooled by 2.97°C, while the SAW, located south of the CR/STF region, cooled by 2.87°C (Shaw et al., 1999). As the CR/STF region is a mixing zone between the SAW and STW (SPSG), it is reasonable to assume that cooling of a similar magnitude also occurred here. 2005 and 2015 were weak El Niño years, and the 2015 weak El Niño was followed by a very strong El
Niño year in 2016; demonstrated by lower SST in the CR/STF region, but not in the SPSG (Fig. 7). In contrast, 2017 and 2018 were each considered weak La Niñas, which are correlated with higher SST around New Zealand (Hopkins et al., 2010). The CR/STF region in 2017-2018 had a significantly higher mean SST of 16.6 ± 0.82°C, than that of the 2015-2016 El Niño years, with a mean SST of 16.0 ± 0.78°C (2-tailed unpaired t-test assuming unequal variances, p = 0.017, a = 0.05). This reflects the hypothesized changes in SST due to ENSO-driven interannual variability in the region.

However, increased SST alone did not drive the increase in Ω between 2015 and 2018, as the results of the sensitivity test showed that changes in SST and SSS together only impacted \( \Omega_{\text{cal}} \) by ≤1%. This is in contrast with work done on the relationship between SST and carbonate parameters in the Gulf of Maine (GoM). In this study, sensitivity tests showed that interannual variability of \( \Omega_{\text{arag}} \) was highest when a model isolated and changed SST and SSS, even more-so than when TA or OA were varied. It is important to note that this study tested pH and \( \Omega_{\text{arag}} \) as dependent variables, so the effect of pH changes on \( \Omega_{\text{arag}} \) was not specifically tested (Salisbury & Jönsson, 2018). However, they assumed that increases in pH were driven by increasing SST and SSS, due to the relative warming of the region (Salisbury & Jönsson, 2018). Therefore, although my sensitivity analyses do not show significant SST- or SSS-driven contributions to changes in \( \Omega_{\text{cal}} \), they may be inherently limited in that they do not quantify what magnitude of the interannual change in pH is caused by interannual changes in SST. For example, in 2017, the CR/STF had the highest SST (Fig. 7), accompanied by increases in both pH (Fig. 9) and TA (Fig. 11) from their 2016 values. 2017 was characterized as a weak La Niña year, characterized by elevated SST in this region (Hopkins et al., 2010). This elevated SST may have decreased air-sea CO₂ flux, as CO₂ is less soluble in warmer waters (Takahashi et al., 2002), which may have
resulted in the high mean pH value for that year. This trend between SST and pH was observed in the 2018 paper by Jönsson and Salisbury (2018). If pH was impacted by SST, then SST was indirectly a stronger driver than our sensitivity tests could have concluded, as pH is the strongest driver of changes in $\Omega$. This may help explain the concurrent increase in all parameters, SST, TA, pH, and $\Omega$ in the 2017 year.

However, an arguably stronger hypothesis than ENSO-driven interannual variability in the CR/STF, is that phytoplankton blooms contributed significantly to the observed changes in the surface carbonate system. Overall trends between 2015 and 2018 in the CR/STF region included a statistically significant decrease in TA, a non-statistically significant increase in pH, and a statistically significant increase in both $\Omega_{\text{cal}}$ and $\Omega_{\text{arag}}$. However, within these overall trends, there were years in which pH and TA tracked together, and years in which they trended in opposite directions. From 2015 to 2016 and from 2017 to 2018, pH increased and TA decreased, but from 2016 to 2017, pH and TA tracked together, both increasing. I propose that in the CR/STF region there were coccolithophore blooms of Emiliania huxleyi, in both 2016 and 2018, when pH and TA had changed in opposite directions from the previous year.

In the CR/STF region, coccolithophore blooms are common (Chang & Northcote, 2016; Law et al., 2018) and interannual variability in pH has been linked to the relative strength and timing of phytoplankton blooms (Longhurst, 2007; Chiswell, 2015; Law et al., 2018). The “Great Calcite Belt” is the area in which coccolithophores tend to bloom in highest abundance (Balch et al., 2011). In the southern hemisphere, this region is largely within the subantarctic waters of the Southern Ocean (Hernández et al., 2018), between 30°S and 60°S (Balch et al., 2011). The CR/STF region lies directly within this “calcite belt” of 30°S and 60°S, so blooms are spatially probable, and have been observed in austral spring and summer (Chang and Northcote, 2016).
This observation is reflected by what is known about the ecological niche of coccolithophores; they prefer waters which are seasonally stratified and tend to bloom around the peak of that stratification, in summer, when light intensity is highest (Balch et al., 2011). All data used in this paper were from austral autumn in April, just after the tail-end of the most likely time for a coccolithophore bloom to occur. However, the TA signature of a major coccolithophore bloom may be left in the surface ocean for days or even weeks after the end of a bloom (Bates et al., 1996).

Biogeochemically, coccolithophore blooms are also supported in 2016 and 2018. Between 2015 and 2016 and between 2017 and 2018, pH increased while TA decreased. The relatively low mean TA values - 2.28 ± 0.12 meq/L in 2016 from 2.50 ± 0.21 in 2015, and 2.26 ± 0.11 in 2018 from 2.38 ± 0.10 in 2017 - were accompanied by pH values higher than their previous years - 8.06 ± 0.02 in 2016 from 7.98 ± 0.06 in 2015, and 8.17 ± 0.03 in 2018 from 8.14 ± 0.03 in 2017. Therefore, implicating the most likely mechanism responsible for the observed perturbations the carbonate system required that this mechanism force pH and TA in opposite directions. Coccolithophore blooms are a likely candidate for this geochemical signature, as coccolithophore blooms couple carbonate precipitation with NO$_3^-$ supported photosynthesis (Eqn. 8; Tyrrell & Merico, 2004), two processes that, together, could produce the observed trends in pH and TA (Kempe & Kaźmierczak, 1994; Bates et al., 1996).

Coccolithophore blooms lower TA, without changing pH, via their biogenic precipitation of CaCO$_3$ shells, which they form by pulling Ca$^{2+}$ and CO$_3^{2-}$ ions from surrounding seawater (Tyrrell & Merico; 2004). When coccolithophores pull CO$_3^{2-}$ (or HCO$_3^-$) from seawater, the ambient seawater [CO$_3^{2-}$] and/or [HCO$_3^-$] decreases, which in turn decreases TA (Bates et al., 1996), as CO$_3^{2-}$ and HCO$_3^-$ are the largest and second largest contributors to TA (Eqn. 6).
Therefore, a large removal of CO$_3^{2-}$ or HCO$_3^-$ from seawater via coccolithophore calcification would result in decreased TA (Bates et al., 1996), as observed in 2016 and 2018. While calcite precipitation alone does not change pH, a coccolithophore bloom increases pH via its metabolism; when NO$_3^-$ is assimilated into biomass, phytoplankton, including coccolithophores, must concurrently consume protons (Eqn. 8), which lowers the [H$^+$] of the surrounding seawater, and increases its pH (Eqn. 5). This trend is observed in the hypothesized bloom years, 2016 and 2018.

$$106\text{CO}_2 + 16\text{NO}_3^- + \text{HPO}_4^{2-} + 122\text{H}_2\text{O} + 18\text{H}^+ \rightarrow \{\text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P}\} + 138\text{O}_2 \quad \text{(Eqn. 8)}$$

(Stumm & Morgan, 2013).

A coccolithophore bloom would also explain the relative minimums of $\Omega_{\text{cal}}$ and $\Omega_{\text{arag}}$ in 2016 (Fig. 13). If CaCO$_3$ was precipitated en-masse for a major coccolithophore bloom, CO$_3^{2-}$ ions would be pulled out of seawater, thus lowering $\Omega$ (Eqn. 7). However, the high $\Omega_{\text{cal}}$ in 2018 (Fig. 13A) does not track with the observed changes in TA (Fig. 11); TA was low in 2018, which should result in lower $\Omega$’s. I propose that the high $\Omega$’s of 2018 may be the result of 2018’s relatively high pH – higher than that of any other study year (Fig. 9). The mechanism behind why pH is so much higher in 2018 than in 2016 remains unclear. However, SST was also slightly higher in 2018 with a mean value of 16.31 ± 0.57°C, than in 2016 with a mean value of 16.01 ± 0.87°C (Fig. 7), which may contribute to higher pH values in 2018 than in 2016. As stated previously, sensitivity tests indicated that pH has the strongest impact on $\Omega$’s, which is the likely reason why 2018 had $\Omega$’s so much higher than those of 2016 (Fig. 11). Despite remaining questions about the high pH in 2018, given the observed decoupling of the trends in pH and TA
in the surface ocean of the CR/STF region, as well as the fact that these cruises closely followed austral summer, I hypothesize that coccolithophore blooms occurred in 2016 and 2018 and ended less than a month before sampling in the respective years.

In order to affirm the hypothesis that a coccolithophore bloom occurred in 2016 and in 2018 in the CR/STF region, future work should include accessing in situ chl-a and PIC as well as satellite-based estimates of these parameters. Balch et al. (2005) describes the algorithm for detecting coccolithophore presence in the surface ocean, in which the “water-leaving radiance” is detected by satellites. The way in which calcite interacts with light is well-known, such that by using detected radiance values from the surface ocean, a model can calculate the concentration of coccoliths or “PIC” (Balch et al., 2005). These remotely sensed values would support the hypothesis that coccolithophore blooms happened in 2016 and 2018 if PIC concentrations appeared to be relatively high over the CR/STF region in 2016 and 2018, particularly in comparison to the 2015 and 2017 study years.

In order to identify if the 2015 to 2018 period was an extension of a longer trend, carbonate parameter values from 2005 were compared to the mean values of those same parameters over the 2015 to 2018 period. In the SPSG region, between 2005 and the 2015 to 2018 period, there were no statistically significant changes; SST appeared to decrease slightly, pH and TA increased slightly, and Ω increased slightly. In the CR/STF region, between 2005 and the 2015 to 2018 period, pH decreased significantly from 8.10 ± 0.01 in 2005 to a mean value of 8.05 ± 0.09 in the 2015-2018 period. Over this same period, TA increased from 2.30 ± 0.01 in 2005, to a mean value of 2.37 ± 0.18 over the 2015-2018 period (Fig. 14), yet Ω_{cal} and Ω_{arag} still increased. However, what held true in both regions, the CR/STF and SPSG, was that there was significant variability in the 2015-2018 dataset. Depending on the year of interest (2015, 2016,
2017, or 2018) being individually compared to 2005, there were cases in which trends in pH and TA were both positive and negative; pH was lower in both 2015 and 2016 than it was in 2005, but was higher in 2017 and 2018 (Fig. 9) while TA was lower than its 2005 value in both 2016 and 2018, but was higher in 2015 and 2017 (Fig. 11).

The simple fact that 2005 values of all parameters fell within the range of 2015-2018 values highlights that there is not one simple trend pushing all parameters in the same direction over the study period (2005-2018). This discrepancy between trends within the 2015-2018 period and between 2005 and the mean of this latter period, further confounds the process of elucidating specific mechanisms in interannual variability. One of the main constraints of this study is lack of a long-term dataset; the data used in this study was from four consecutive years and one additional year. Because values of carbonate parameters from the outside year – 2005 - fell within the ranges of values seen in the 2015-2018 period, the overall trends between the two datasets are less helpful in identifying mechanisms that produce interannual variability. Not explored in this study is the possibility of cycling in the mechanisms presented and resulting perturbations to the carbonate system in the region over decadal timescales. The Pacific Decadal Oscillation (PDO) is important in this region (Mantua & Hare, 2001) but there simply are not nearly enough years of data to make claims about changes over decadal timescales.

5. CONCLUSION

This study quantified interannual variability in surface ocean carbonate chemistry over the 2015 to 2018 period and between the 2005 and 2015 through 2018 period. The main variables of interest, $\Omega_{cal}$ and $\Omega_{arag}$ did not change significantly in the SPSG, but appear to change significantly due to interannual mechanisms in the CR/STF region. ENSO cycles may contribute to changes in the SST and carbonate parameters, particularly if changes in SST drive changes in
pH. However, the main hypothesized driver of changes in carbonate parameters in the CR/STF was productivity, specifically NO$_3^-$-supported photosynthesis by coccolithophores because these blooms would leave a signature of decreased TA and increased pH, which was observed in 2016 and 2018 in the CR/STF region. In future work, this hypothesis should be substantiated using *in situ* and/or satellite chl-a and PIC measurements. In the SPSG region, mechanisms behind interannual variability were more difficult to identify, but ENSO-driven changes seemed more likely to be playing a role in the northern sub-region than in the southern sub-regions.

This study did not elucidate all mechanisms behind interannual variability in all sub-regions for all study years. However, it did successfully provide observational constraints on the range in carbonate parameters in the study region over a four-year time scale, thus contributing to the establishment of a “baseline” for the region. This is crucial for differentiating natural variability from anthropogenic-driven impacts to regional carbonate chemistry. A future question highlighted by this study is whether or not $\Omega$ may dip below critical values in this region earlier than prior estimates predict due to the high magnitude of “noise” on either side of OA’s decreasing trend. In this study, $\Omega$ never dipped close to a value of 1, but considering that $\Omega_{cal}$ and $\Omega_{arag}$ can vary from 10-25% over a four-year period, I am concerned that even a well-constrained OA trend in $\Omega$ may not predict short periods of undersaturation preceding the sustained undersaturation that we expect to see in coming decades. In order to constrain the magnitude and frequency of this interannual cycling, more years of data collection are needed, but it is an important cautionary consideration when estimating the fate of calcifying organisms in the coming decades.
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