



GEOSCIENCES

The marine carbonate system along the northern Antarctic Peninsula: current knowledge and future perspectives

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Abstract: Among the regions of the Southern Ocean, the northern Antarctic Peninsula (NAP) has emerged as a hotspot of climate change investigation. Nonetheless, studies have indicated issues and knowledge gaps that must be addressed to expand the understanding of the carbonate system in the region. Therefore, we focused on identifying current knowledge about sea-air CO_2 fluxes (FCO_2), anthropogenic carbon (C_{ant}) and ocean acidification along NAP and provide a better comprehension of the key physical processes controlling the carbonate system. Regarding physical dynamics, we discuss the role of water masses formation, climate modes, upwelling and intrusions of Circumpolar Deep Water, and mesoscale processes. For FCO_2 , we show that the summer season corresponds to a strong sink in coastal areas, leading to CO_2 uptake that is greater than or equal to that of the open ocean. We highlight that the prevalence of summer studies prevents comprehending processes occurring throughout the year and the net annual CO_2 balance in the region. Thus, temporal investigations are necessary to determine natural environmental fluctuations and to distinguish natural variability from anthropogenically driven changes. We emphasize the importance of more studies regarding C_{ant} uptake rate, accumulation, and export to global oceans.

Key words: CO_2 fluxes, anthropogenic carbon, ocean variability, carbon cycle, Southern Ocean, biogeochemistry.

INTRODUCTION

The Southern Ocean connects global ocean circulation and, thus, plays a key role in biogeochemical cycles and exchanges of properties across the compartments of the earth system and ocean basins. This role has implications for the global climate through: (i) upwelling of deep waters returning nutrients to support biological productivity on the surface (Rintoul 2011); (ii) ocean uptake of huge amounts of carbon dioxide (CO_2) from the atmosphere and its transfer and storage in the interior of oceans (e.g., Landschützer et al. 2015); and (iii)

oxygenation of deeper layers of the oceans through ocean ventilation processes (Talley et al. 2011). This last process also acts to sequester carbon and absorb heat on the ocean surface to deep levels.

The northern Antarctic Peninsula (NAP) has drawn the attention of the scientific community as a key region for climate change studies (e.g., Kerr et al. 2018a, Henley et al. 2019). It lies in a transition zone between sub-polar and polar regions and has a set of unique marine environments under the influence of distinct ocean processes and climate stressors, encompassing the Bransfield Strait,

the Gerlache Strait, the northwestern Weddell Sea, and the south portion of the Drake Passage (Figure 1a). These environments have revealed high sensitivity to climate change, exhibiting ice loss caused by ice-shelf collapsing (Shepherd et al. 2018) and alterations to physical (e.g., Azaneu et al. 2013, Dotto et al. 2016, Hellmer et al. 2016, Collares et al. 2018) and biogeochemical (e.g., Lencina-Avila et al. 2018, Henley et al. 2020) characteristics and, consequently, to the marine biota (e.g., Mendes et al. 2013, 2018a, b, Seyboth et al. 2018, Ferreira et al. 2020). Thus, studies conducted along NAP ecosystems allow climate-induced responses of processes to be observed even in a short period of time (e.g., Vaughan et al. 2003, Gonçalves-Araújo et al. 2015, Kerr et al. 2018a, b) and, thus, are relevant to strengthening the comprehension achieved by global biogeochemical research.

From a biogeochemical perspective, the environments around NAP were first studied regarding sea-air CO_2 flux (FCO_2) through the FRUELA project (Álvarez et al. 2002, Anadón & Estrada 2002). Most recently, NAP was investigated through direct and indirect measurements of carbonate system parameters (e.g., Ito et al. 2018, Kerr et al. 2018c, d, Lencina-Avila et al. 2018). The magnitude and spatiotemporal variability of FCO_2 were investigated together with the environmental factors that regulate carbon biogeochemistry (primary production, nutrients concentration, etc.; e.g., Ito et al. 2018, Kerr et al. 2018c, Monteiro et al. 2020a, b). The acidification state and the amount of anthropogenic carbon (C_{ant} – i.e., the human emitted atmospheric CO_2 – released from different processes, such as fossil fuel combustion, industry, agricultural and land management) storage at NAP waters have also been monitored (Kerr et al. 2018d, Lencina-Avila et al. 2018). Even though efforts are being made to improve knowledge of such issues of the marine carbonate system, it is important

to note that biogeochemical studies at NAP are quite scarce compared to other Southern Ocean regions (e.g., western Antarctic Peninsula). Continuous long-term monitoring of carbonate system parameters is still required and an evaluation of biogeochemical research priorities is needed to advance on research questions and serve as a guideline for future investigation.

Here we present the current state of knowledge regarding the marine carbonate system along NAP and its surroundings and address major questions in need of attention of the scientific community. Such questions are related to logistical, infrastructure, and scientific issues and are mainly discussed through physical and biological aspects that control the biogeochemical processes of FCO_2 , C_{ant} distribution, and ocean acidification. In this context, we also shed light on applicable future investigations and key questions that represent scientific challenges in the region. We also present a seasonal overview of the carbonate system of NAP based on observational data of CO_2 partial pressure ($p\text{CO}_2$) from SOCAT version 2020 (Bakker et al. 2016) and the hydrographic collection surveyed by the Brazilian High Latitude Oceanography Group (GOAL) along NAP for almost 20 years (e.g., Mata et al. 2018, Dotto et al. 2021). The GOAL biogeochemical collection has been boosted by the increase in carbonate system parameters measured by the group during the last 10 years (Figure 1b; e.g., Ito et al. 2018, Kerr et al. 2018c, d, Lencina-Avila et al. 2018, Monteiro et al. 2020a, b).

The northern Antarctic Peninsula as a climate change hotspot

One of the key regions of NAP is the Bransfield Strait, which has emerged as a strategic proxy region for climate change investigation with relatively easy access and restricted connections to the surroundings (e.g., Dotto et al. 2016, Damini

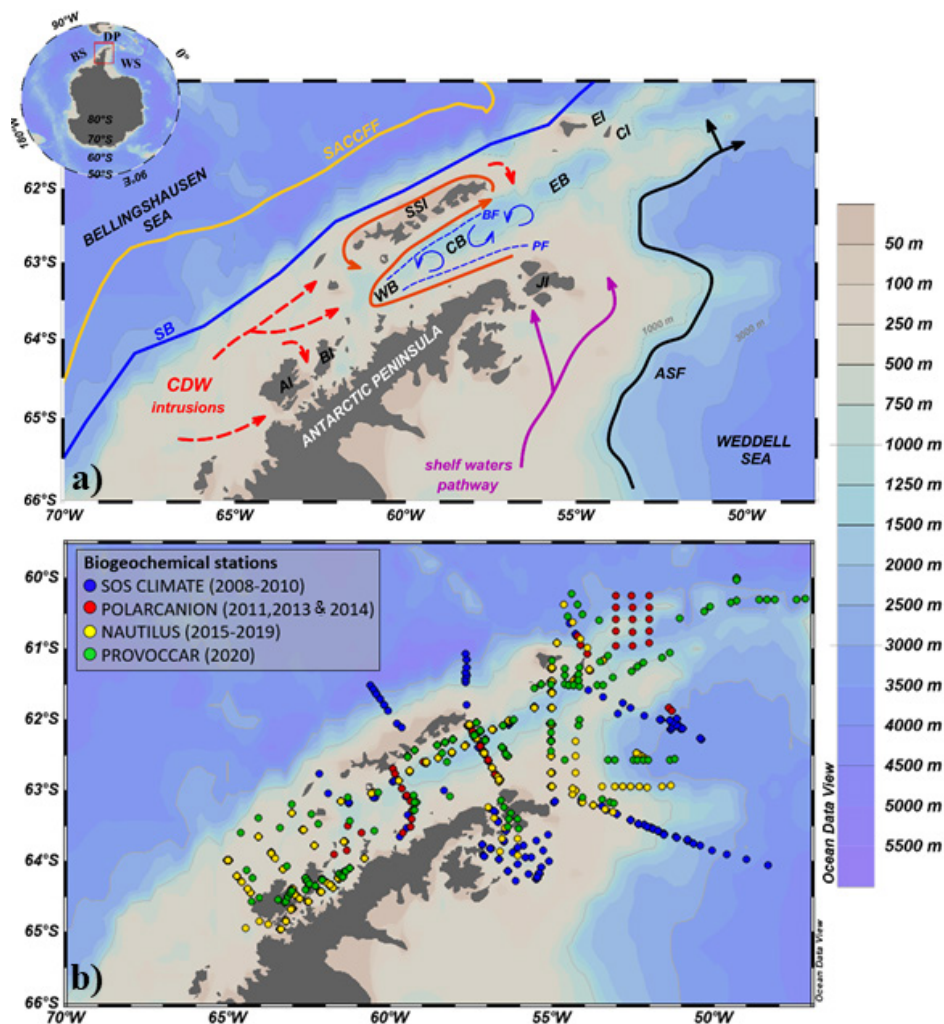


Figure 1. a) Schematic representation of ocean circulation and front patterns along the northern Antarctic Peninsula and its surroundings. Arrows represent the pathways of Circumpolar Deep Water (CDW) intrusions (dashed red; Dotto et al. 2016, Ruiz Barlett et al. 2018) and Weddell Sea Dense Shelf Waters advection (continuous purple) entering NAP. Yellow and blue lines represent mean locations of the Southern Antarctic Circumpolar Current Front (SACC) and the Southern Boundary (SB) of the Antarctic Circumpolar Current, respectively, following Orsi et al. (1995). Mesoscale eddies along the Bransfield Strait are shown by blue arrows. Black arrows represent the mean location of the Antarctic Slope Front (ASF; Heywood et al. 2004, Azaneu et al. 2017). The orange arrow denotes the Bransfield Current System (Sangrà et al. 2011, 2017). Dashed blue lines indicate the Peninsula Front (PF) and the Bransfield Front (BF). The Bransfield Strait basins are indicated as Western Basin (WB), Central Basin (CB) and Eastern Basin (EB). The islands are: Anvers Island (AI), Brabant Island (BI), Clarence Island (CI), Elephant Island (EI), Joinville Island (JI) and South Shetland Islands (SSI). **b)** Brazilian High Latitude Oceanography Group (GOAL) biogeochemical stations at NAP over the years 2008–2020. The colored dots represent the biogeochemical stations of the respective scientific projects: SOS-CLIMATE 2008–2010 (blue); POLARCANION 2011, 2013, 2014 (red); NAUTILUS 2015–2019 (yellow), and PROVOCCAR 2020 (green). The SOS-CLIMATE includes measurements of dissolved macronutrients and oxygen, pH, and $p\text{CO}_2$ continuous survey. Only dissolved macronutrients and oxygen were measured during the POLARCANION survey, with the addition of pH during the 2014 cruise. NAUTILUS and PROVOCCAR surveys encompass the same measurements as SOS-CLIMATE, including sampling of total alkalinity, total dissolved inorganic carbon, and particulate, dissolved and total organic carbon. Phytoplankton pigments and functional groups were measured during all cruises. NAUTILUS 2016 and 2019 includes $p\text{CO}_2$ continuous survey. The GOAL biogeochemical dataset is provided by request.

et al. 2022). This strait has become a climate change hotspot due to both the hydrographic characteristics of the water masses preserved in the region (Hofmann et al. 1996, Wilson et al. 1999, Gordon et al. 2000, Garcia & Mata 2005), and the effect of temperature on gas solubility (i.e., lower temperatures increase CO_2 solubility; Kerr et al. 2018c). It is a semi-closed ocean basin located at NAP (Figure 1; López et al. 1999, Kerr et al. 2018a) with three deep basins (i.e., western, central, and eastern) separated by relatively shallow sills (Gordon & Nowlin Jr 1978). The varieties of Dense Shelf Water that are formed in the Weddell Sea continental shelf sink into the central and eastern basins of the Bransfield Strait and can be retained at great depths. Because of little mixing with adjacent waters during downward cascade, most of the climate signals of recent changes present in the Dense Shelf Water are preserved (Dotto et al. 2016, van Caspel et al. 2018, Damini et al. 2022). Thus, the deep basins of the Bransfield Strait provide excellent conditions for studies of climate impacts on marine biogeochemistry across NAP.

Diverse studies have characterized carbonate system parameters (i.e., pH, $p\text{CO}_2$, total alkalinity – TA, and total dissolved inorganic carbon – DIC) around NAP, mainly in the Gerlache Strait (Álvarez et al. 2002, Anadón & Estrada 2002, Kerr et al. 2018a, b, Lencina-Avila et al. 2018). Moreover, contributions regarding FCO_2 in the Weddell Sea (van Heuven et al. 2014) and in Gerlache and Bransfield Straits (Álvarez et al. 2002, Anadón & Estrada 2002, Ito et al. 2018, Kerr et al. 2018c, Costa et al. 2020) have reported sinking behavior for atmospheric CO_2 during summer periods. The Gerlache Strait has recently been reported as a region of intensified CO_2 absorption in summer (Monteiro et al. 2020a), while it acts as a moderate to strong CO_2

source to the atmosphere during autumn and winter (Monteiro et al. 2020b).

Although the carbonate system at the Bransfield Strait remains not yet fully constrained, it is known that collapsed ice shelves release an excess of meltwater in the Weddell Sea (Paolo et al. 2015, Cook et al. 2016, Shepherd et al. 2018, Rignot et al. 2019). Thus, this excess of meltwater on the ocean surface can affect seawater properties of the Bransfield Strait (Dotto et al. 2016, Ruiz Barlett et al. 2018). Signals of cooling, freshening, and lightening of the deepest and most stable layers of the Bransfield Strait have already been identified by several studies for periods over at least the past 50 years (e.g., Garcia & Mata 2005, Azaneu et al. 2013, Schmidtke et al. 2014, Dotto et al. 2016, Ruiz Barlett et al. 2018, Damini et al. 2022). However, a signal of freshening reversal was observed in the deep central and eastern basins after the 2010s, which was associated with increased input of Dense Shelf Water, formed in the Weddell Sea, into the Bransfield Strait (Damini et al. 2022). Thus, the impact of each of these high freshwater inputs on the carbonate system must be investigated, as they can directly influence TA and CO_2 solubility. In addition, future studies should explore how these increased inputs of CO_2 -rich Dense Shelf Water will affect the acidification state of the Bransfield Strait.

CO₂-carbonate system data

In this section we explore seawater $p\text{CO}_2$ measurements from SOCAT version 2020 (Bakker et al. 2016), and the seasonal GOAL gridded dataset for NAP (Dotto et al. 2021), to examine $p\text{CO}_2$ and TA along the NAP environments.

As for other coastal regions around Antarctica, the biogeochemical properties of NAP are relatively under-sampled, which precludes a better understanding of the dynamics of its marine carbon cycle. This is particularly true for

carbonate system parameters other than $p\text{CO}_2$ (Arrigo et al. 2008, Kerr et al. 2018c, d, Monteiro et al. 2020a, b). Thus, here we use seawater $p\text{CO}_2$ surface measurements from SOCAT version 2020 (Bakker et al. 2016), to explore the seasonal distribution of $p\text{CO}_2$ along NAP (Figure 2). Summer average seawater $p\text{CO}_2$ was $327.2 \pm 61.4 \mu\text{atm}$ for 2000–2009 and $328.1 \pm 69.6 \mu\text{atm}$ for 2010–2019, considering the eastern and western

portions of NAP. However, considering only the western portion, the average $p\text{CO}_2$ increases to $344.7 \pm 46.6 \mu\text{atm}$ for 2000–2009 and to $333.4 \pm 67.9 \mu\text{atm}$ for 2010–2020. In summer, $p\text{CO}_2$ is lower in the eastern (Weddell Sea) and southern (Bellingshausen Sea) portions of NAP, while it is homogeneously higher in the other areas (Figure 2). The maximum $p\text{CO}_2$ is reached in winter and the difference between 2000–2009 (410.9 ± 34.4

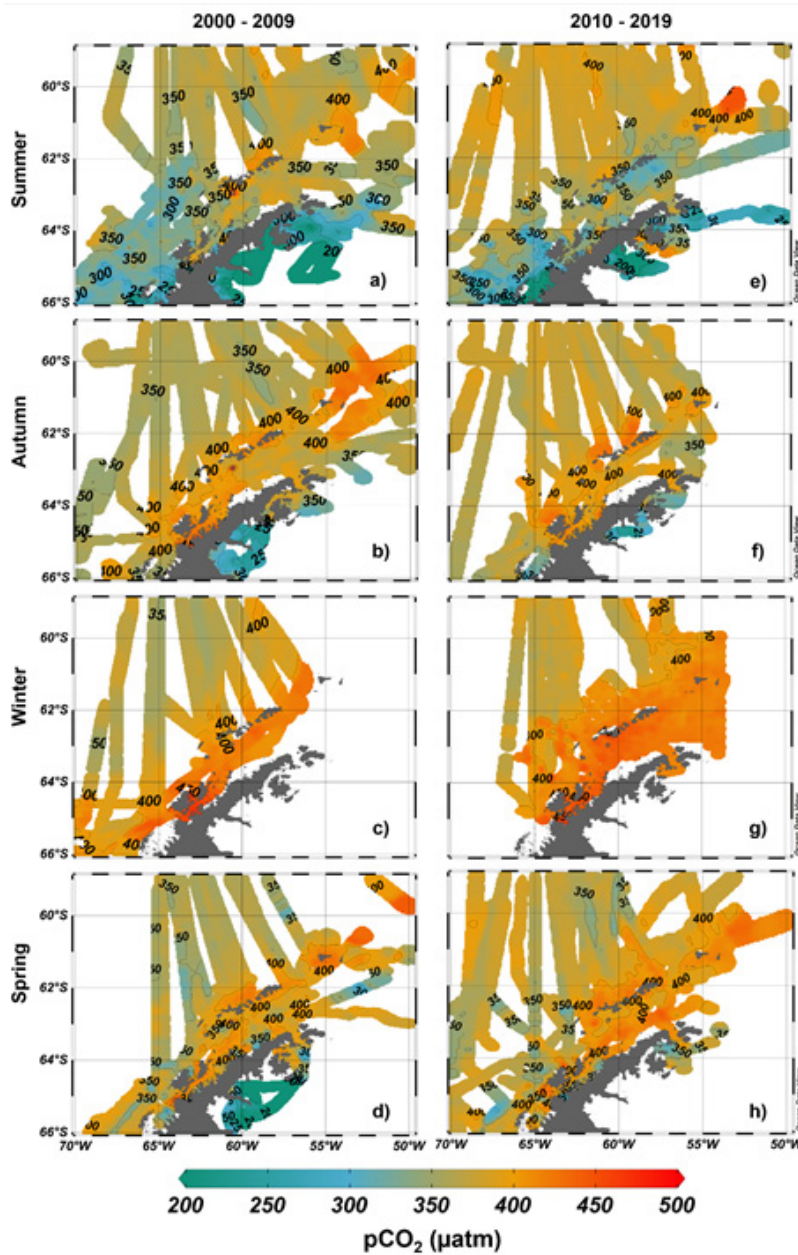


Figure 2. Seasonal distribution of seawater CO_2 partial pressure ($p\text{CO}_2$ in μatm) along the northern Antarctica Peninsula. Observed dataset extracted from SOCAT version 2020 (Bakker et al. 2016) for the decadal periods of (a-d) 2000–2009 and (e-h) 2010–2020. The computed seasonal periods were austral summer (JFM), autumn (AMJ), winter (JAS) and spring (OND).

μatm) and 2010–2019 ($415.3 \pm 24.6 \mu\text{atm}$) may be due to the greater spatial coverage of the 2010–2019 data. The spatial distribution and average $p\text{CO}_2$ are similar between autumn and spring. The difference in average $p\text{CO}_2$, considering or not the eastern portion, is smaller than in summer. The autumn average $p\text{CO}_2$ was $383.8 \pm 40.4 \mu\text{atm}$ for 2000–2009 and $389.5 \pm 31.0 \mu\text{atm}$ for 2010–2019 (for the entire region). The spring average $p\text{CO}_2$ was $385.9 \pm 43.3 \mu\text{atm}$ for 2000–2009 and $389.2 \pm 53.5 \mu\text{atm}$ for 2010–2019 (for the entire region). The east of NAP is subsampled throughout the year, and is completely unsampled in winter

(Figure 2c, g). Therefore, the Weddell Sea to the east of NAP is a priority region for $p\text{CO}_2$ sampling throughout the year, and primarily in the winter period. On the other hand, the west of NAP should be sampled, mainly in winter, to better understand the seasonal dynamics of $p\text{CO}_2$.

The magnitude of the amount of $p\text{CO}_2$ data along NAP is disproportionate among seasons (Figure 3), which impairs understanding the seasonal carbon cycle in this region. From 2000 to 2020, $p\text{CO}_2$ sampling across NAP regions was more consistent during the summer, when the amount of data was greater than 10,000

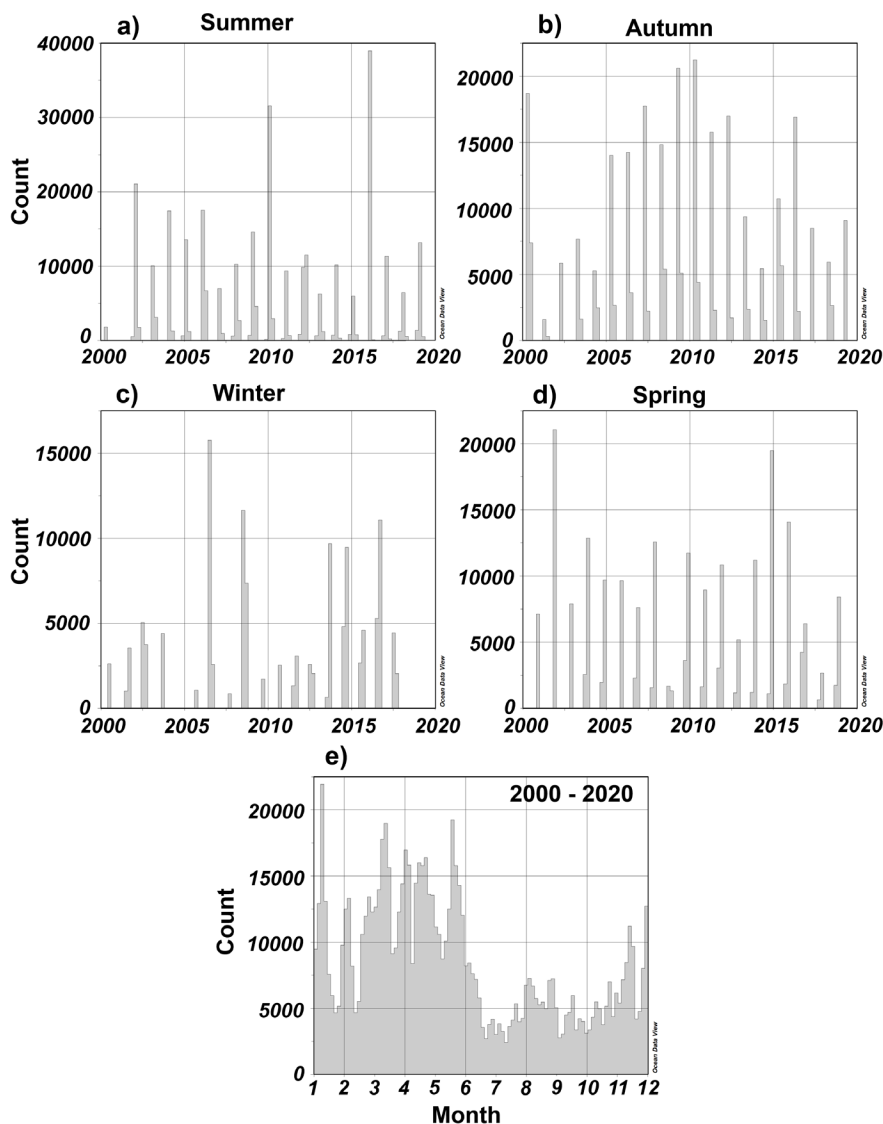


Figure 3. Histogram showing the amount of continuous surface data of CO_2 partial pressure, temperature, and salinity along the northern Antarctica Peninsula (a-d) seasonally and (e) compiled for the entire period (data presented in Figure 2) during 2000–2020. Note that the magnitude of the amount of data (y-axis) differs among graphs.

measurements in most years (Figure 3a). This consistency decreases in autumn (Figure 3b) and spring (Figure 3d) and is drastically lower in winter with the amount of data being less than 10,000 measurements in most of the 20 years (Figure 3c). The disproportion amount of $p\text{CO}_2$ data is even more evident among the months of the year (Figure 3e), with July being the least sampled month with less than 5,000 data for the past 20 years.

Although $p\text{CO}_2$ data covers west of NAP environments relatively well (Álvarez et al. 2002, Anadón & Estrada 2002, Ito et al. 2018, Kerr et al. 2018c, Costa et al. 2020), mainly during summer, the understanding of the biogeochemical processes involved in carbon dynamics remains regionally limited (e.g., Monteiro et al. 2020a, b) by the absence of data for other carbonate system parameters. For example, changes in TA and DIC can provide information relevant to understand carbon dynamics (Takahashi et al. 2014, Hauri et al. 2015, Brown et al. 2019, Monteiro et al. 2020a, b). Therefore, efforts have been made to fill these gaps by estimating parameters that are known to be related to the most frequently available variables (e.g., sea surface salinity – SSS and temperature – SST). For instance, TA is widely estimated by linear or polynomial correlation with SSS and/or SST (Lee et al. 2006, Carter et al. 2018). Lee et al. (2006) proposed equations to estimate TA, which are widely used in the global ocean and in the Southern Ocean. However, specific equations for TA estimations, mainly for coastal regions, present smaller errors than those of Lee et al (2006). For example, Lencina-Avila et al. (2018) proposed equations to estimate TA and DIC along the mixed layer (< 60 m) in the Gerlache Strait. However, since those values were outside the expected range for the surface, they were excluded from the present analysis. Hauri et al. (2015) estimated TA as $\text{TA} = 57.01 \times \text{SSS} + 373.86$ ($r^2 = 0.77$; $\text{RMSE} = 15.2$

$\mu\text{mol kg}^{-1}$) for the summer in south of NAP, which was later used in other studies in that region (e.g., Brown et al. 2019). Similarly, Monteiro et al. (2020a) proposed an estimate from SSS and SST as $\text{TA} = 685.34 + 3.95 \times \text{SST} + 47.91 \times \text{SSS}$ ($r^2 = 0.45$; $\text{RMSE} = 16.8 \mu\text{mol kg}^{-1}$) for summer in the Gerlache Strait. Finally, Monteiro et al. (2020b) proposed an estimated TA for the seasonal cycle in the Gerlache Strait as $\text{TA} = 36.72 \times \text{SSS} + 1052$ ($r^2 = 0.98$; $\text{RMSE} = 4.4 \mu\text{mol kg}^{-1}$). Despite providing a smaller error than previous models (i.e., Hauri et al. 2015, Monteiro et al. 2020a), the data used to construct and validate the equation of Monteiro et al. (2020b) were restricted to the summer period. Assuming that TA has a wide range of variability in the summer, they used this same approximation to estimate TA throughout the year. Applying the approaches of Lee et al. (2006) and Monteiro et al. (2020b) to a seasonal hydrographic gridded dataset for NAP (Dotto et al. 2021), we observed that they generate similar distributions of TA and are, thus, able to show the gradient used to split the waters characteristic of the Bellingshausen and Weddell Seas (Figure 4). This separation cannot be seen by the Monteiro et al. (2020a) approach. As they are all estimates, when we assume the approach of Lee et al. (2006) as a reference we see that the approximation of Monteiro et al (2020b) is more consistent with it and that those by Hauri et al. (2015) and Monteiro et al. (2020a) overestimate TA (Figure 4). For example, the approximation of Monteiro et al. (2020b) overestimates that of Lee et al. (2006) by at most $5 \mu\text{mol kg}^{-1}$ in summer and underestimates by at most $6 \mu\text{mol kg}^{-1}$ in winter. The other approximations (Hauri et al. 2015, Monteiro et al. 2020a) overestimate by at least $10 \mu\text{mol kg}^{-1}$ during almost the entire year. However, it is still necessary to expand this analysis beyond summer to make sure that the relationship between TA and SSS and/or SST is consistent throughout the year. In addition to

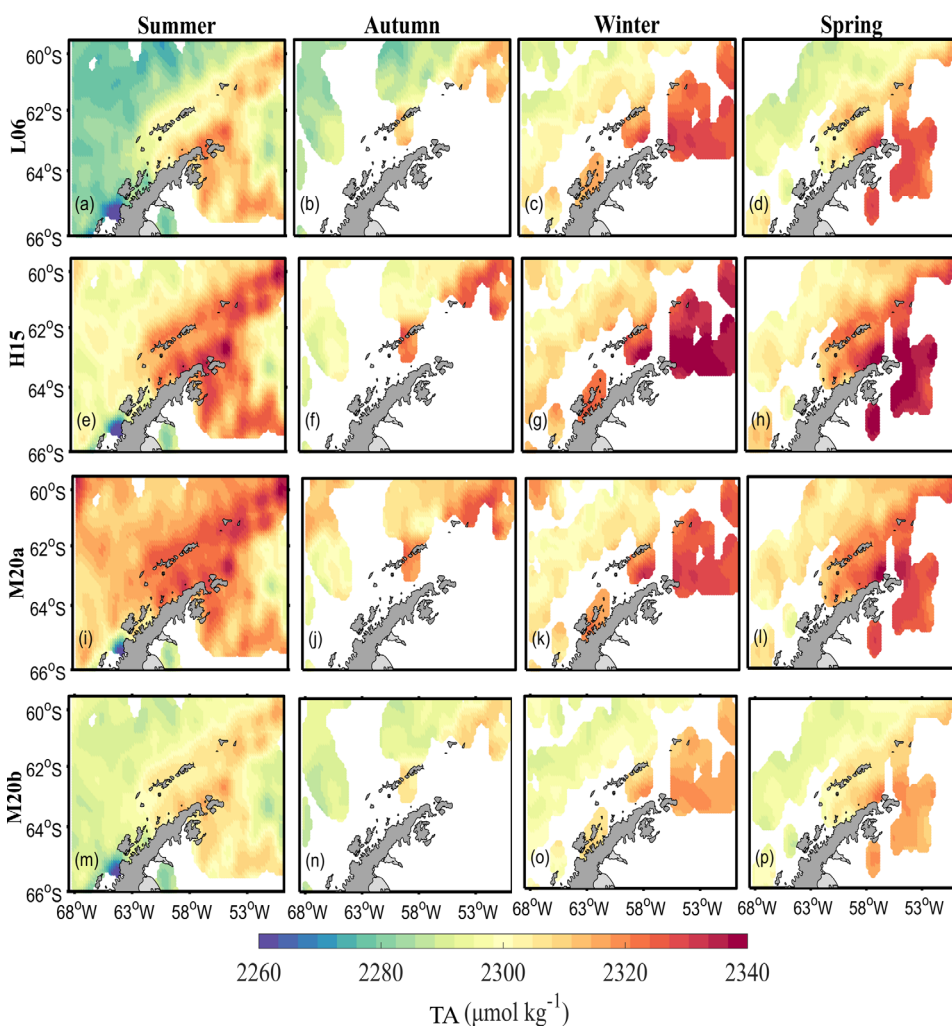


Figure 4. Surface distribution of total alkalinity (TA in $\mu\text{mol kg}^{-1}$) estimated by TA algorithms proposed for along the Northern Antarctica Peninsula (NAP). The algorithms were applied on the seasonal hydrographic gridded dataset for NAP by Dotto et al. (2021). The algorithms are: (a-d) Lee et al. (2006) – L06; (e-h) Hauri et al. (2015) – H15; (i-l) Monteiro et al. (2020a) – M20a; and (m-p) Monteiro et al. (2020b) – M20b.

a consistent estimate of TA, a robust approach to estimate DIC on the surface of NAP would considerably broaden our understanding of carbon dynamics by enabling the calculation of the other parameters of the carbonate system. Importantly, these approximations of TA are restricted to the surface (< 5m) and do not consider the mixed layer.

Ocean processes controlling carbonate system distribution and variability

An intense mixture of water masses, especially at the Bransfield Strait, shapes the physical environment of NAP, which encompasses oceanic and coastal ecosystems (Sangrà et al. 2011).

This region is strongly influenced by intrusions of Dense Shelf Water from the Weddell Sea (Dotto et al. 2016, van Caspel et al. 2018, Barillet et al. 2018, Damini et al. 2022) and Circumpolar Deep Water from the Antarctic Circumpolar Current (Barillet et al. 2018, Moffat et al. 2018). Atmospheric and oceanic teleconnections are responsible for interannual variability in carbonate system parameters (Dotto et al. 2016, Avelina et al. 2020, Damini et al. 2022). Moreover, mesoscale and submesoscale features add complexity to the hydrography and circulation along NAP (Zhou et al. 2002). These physical environmental conditions, together with anthropogenic impacts (e.g., climate change

driven ice-shelf collapsing; water masses freshening and lightening; CO₂ emissions from its multiple sources and consequent uptake by the ocean), act to modulate carbonate system properties and, consequently, sea-air exchange of CO₂ along NAP (Ito et al. 2018, Kerr et al. 2018c, d, Monteiro et al. 2020a, b). However, the biogeochemical responses of the carbonate system to climate-induced physical alterations at NAP (i.e., intensification of westerlies, warming temperature, melting of sea ice and glaciers, etc.) are still under investigation (Kerr et al. 2018c, d, Lencina-Avila et al. 2018, Monteiro et al. 2020a, b). Here, we address the physical aspects and the anthropogenic-driven changes likely to have a significant effect on the distribution and variability of carbonate system parameters.

Processes of water masses formation

The Weddell Sea has stood out as a critical area for C_{ant} uptake in the Southern Ocean (e.g., Hoppema 2004, Tréguer & Pondaven 2002), counteracting with outgassing of CO₂ driven by the upwelling of carbon-rich deep water. The formation of water masses is responsible for permanent C_{ant} uptake since the C_{ant} is conducted to the oceans interior when the water masses sink and then transport it throughout the world's oceans (e.g., Pardo et al. 2014). However, climate-driven changes within the Weddell Sea may eventually impact Antarctic Bottom Water formation, causing changes in global thermohaline circulation (Purkey & Johnson 2010) and affecting carbon transfer among ocean basins.

The northwestern Weddell Sea, where the formation and export of deep waters to the global ocean take place, has a great influence on the eastern boundary of NAP (Ferreira & Kerr 2017, Kerr et al. 2018b). Changes in ocean ventilation processes have been reported in the Atlantic sector of the Southern Ocean leading to further sequestration of C_{ant} in the Antarctic

Intermediate Water (Tanhua et al. 2016). Moreover, C_{ant} changes in the Antarctic Intermediate Water revealed ongoing a rapid acidification process (Salt et al. 2015, Carvalho-Borges et al. 2018, Orselli et al. 2018), with potential to significantly impact primary productivity and the carbon cycle over long timescales (Panassa et al. 2018). Increased nutrient concentration in the Weddell Gyre (Hoppema et al. 2015) has been linked to increased DIC concentrations in bottom water (van Heuven et al. 2014). These gradual changes to nutrient and carbon concentrations in the Atlantic sector of the Southern Ocean are prone to affect the balance of the carbonate system at NAP. However, an investigation into how nutrient and DIC concentrations have changed at NAP is still lacking. Logistical difficulties involved in oceanographic surveys and monitoring, especially during winter, still hamper the investigation of water masses formation processes in NAP and their consequences for the biogeochemical carbon cycle.

The influence of climate mode signals on the carbonate system

Large-scale climate modes of variability, such as El Niño-Southern Oscillation (ENSO) and Southern Annular Mode (SAM), have been identified as the main drivers of interannual changes in hydrographic (Dotto et al. 2016, Ruiz Barlett et al. 2018, Damini et al. 2022) and biogeochemical properties (Avelina et al. 2020, Dinniman et al. 2012, Keppler & Landschützer 2019) of NAP. These climate modes play important roles in the variability of surface carbonate on interannual and shorter time scales (L'Heureux & Thompson 2006, Verdy et al. 2007, Lovenduski et al. 2007, 2008, Le Quéré et al. 2007, Lenton et al. 2009).

During the positive phase of ENSO (El Niño), both the Southern Antarctic Circumpolar Current Front and the Southern boundary of the Antarctic

Circumpolar Current are displaced further north, moving less Circumpolar Deep Water into NAP (Ruiz Barlett et al. 2018). Conversely, during the negative phases of ENSO (La Niña), the northwesterly winds are strengthened and more frequent (Yuan 2004), and the Southern Antarctic Circumpolar Current Front and the Southern boundary of the Antarctic Circumpolar Current shift towards the Antarctic Peninsula, moving more Circumpolar Deep Water into NAP (Loeb et al. 2010, Ruiz Barlett et al. 2018).

Throughout the positive SAM phase, stronger westerly winds shift the position of the Southern Antarctic Circumpolar Current Front and the Southern boundary of the Antarctic Circumpolar Current towards the Antarctic Peninsula (Marshall et al. 2004, Renner et al. 2012), which brings Circumpolar Deep Water towards the western side of NAP. Besides, both the Antarctic Slope Current and the Weddell Gyre are intensified, limiting the connection between the Weddell Sea and NAP (Renner et al. 2012, Youngs et al. 2015) and allowing the advection of Dense Shelf Water from the Weddell Sea into NAP (Dotto et al. 2016, Damini et al. 2022). Contrarily, during the SAM negative phase, weaker westerly winds displace the Southern boundary and the Southern Antarctic Circumpolar Current Front further north, weakening the Weddell Gyre and Antarctic Slope Current circulations, thereby enabling the transport of Weddell Sea Dense Shelf Water varieties into NAP (Dotto et al. 2016, van Caspel et al. 2018, Damini et al. 2022).

Regarding biogeochemistry, stronger westerly winds caused by the positive SAM phase modify turbulence, affecting oceanic carbon uptake in some regions of the Southern Ocean (Nevison et al. 2020). Meanwhile, ENSO can influence the acidification state of NAP due to the increased mixture of Circumpolar Deep Water with the Dense Shelf Water advected from the Weddell Sea, leading to more (less)

CO₂ uptake during the positive (negative) phase (Brown et al. 2019, Avelina et al. 2020, Costa et al. 2020). Studies suggest the occurrence of extreme ENSO events in the future (up to two-fold, according to models CMIP3 and CMIP5) (Cai et al. 2014, 2018), and the SAM trend is expected to remain positive (Marshall 2003). If this truly happens, we may observe more atmospheric CO₂ uptake and associated ocean acidification in the region. However, the influence of ENSO and SAM changing the carbonate system parameters still puzzles the scientific community, with some studies bringing apparently contradictory conclusions, such as the SAM positive phase enhancing CO₂ outgassing (e.g., Lovenduski et al. 2007), or CO₂ drawdown due to biological processes overlooked throughout seasons (e.g., Hauck et al. 2013). Additionally, a persistent positive phase of the SAM index will increase eddy formation in the ocean, conversely, it will contribute to deepening the summer upper mixed layer and reducing phytoplankton biomass and productivity (Leung et al. 2015). The coupled influence of changes in the upper mixed layer, available photosynthetic active radiation, the SAM effects over the ocean, and deglaciation processes around the NAP are expected to significantly alter the composition and size of the phytoplankton community (Ferreira et al. 2020). Thus, also leading to impact the natural variability and distribution of the carbonate system parameters in the studied region.

Circumpolar Deep Water upwelling as a trigger to changing carbonate system parameters

Circumpolar Deep Water intrusions (Moffat et al. 2009, Moffat & Meredith 2018, Henley et al. 2019) are recognized as influencing the carbonate system along NAP environments (Legge et al. 2015, 2017, Lencina-Avila et al. 2018, Monteiro et al. 2020a, b, Moore et al. 2013, 2018) by the increased supply of macronutrients and CO₂

to subsurface shelf waters, but the extension of such influence remains unquantified. The entrainment and upwelling of Circumpolar Deep Water (DIC-rich and carbonate-poor) into the surface layer lowers the carbonate concentration considerably (McNeil & Matear 2008). Actually, the upwelling of deep CO₂-rich waters, such as Circumpolar Deep Water, into NAP is the most dominant driver of winter carbon cycling when compared to temperature-driven differences in solubility or biological processes (McNeil et al. 2007, Takahashi et al. 2014). However, the dimension of these changes to carbonate properties will vary depending on mixing processes in response to sea ice, eddies formation, topography, and atmospheric forces (Henley et al. 2019, Brearley et al. 2019). Some recent studies have reported these mechanisms in the continental shelves and coasts of the western Antarctic Peninsula (Legge et al. 2015, 2017, Jones et al. 2017, Henley et al. 2019).

An investigation of DIC, TA, and pCO₂ in southern NAP presented no significant trends (1993–2012) in DIC dynamics during summer seasons (Hauri et al. 2015). Nevertheless, the long-term reduction of sea-ice coverage, leading to increased CO₂- and nutrient-rich Circumpolar Deep Water upwelling, may enhance CO₂ outgassing in winter and reduce biological uptake in summer (Legge et al. 2015, Brown et al. 2019, Cape et al. 2019). Large uncertainties still hover over the impacts of physical aspects on sea-air CO₂ exchange and only continuous monitoring will enable better conclusions on the course of carbonate impacts at NAP, which is also linked to better knowledge about the ways and periods of Circumpolar Deep Water intrusions in the studied region (e.g., Moffat et al. 2009, Couto et al. 2017, Wang et al. 2022).

The influence of mesoscale and submesoscale processes on the carbonate system

The combined influence of ocean fluxes derived from the Bellingshausen and Weddell Seas can trigger sharp changes in the physical (i.e., temperature, salinity; Huneke et al. 2016) and biogeochemical (i.e., chlorophyll-a concentration, pCO₂; e.g. van Heuven et al. 2014) properties around NAP, characterizing it as a frontal zone. Among these fronts, we highlight (i) the Bransfield Front and (ii) the Peninsula Front (Figure 1). The Bransfield Front (Figure 1) is located in the subsurface over the continental slope of the South Shetland Islands. This front separates the warm waters flowing along with the Bransfield Current and the cold waters at mid-depths within the deep basins (Grelowski et al. 1986, Niiler et al. 1991, Sangrà et al. 2011, 2017, Zhou et al. 2002, 2006). The Peninsula Front (Figure 1), which is a surface front that extends up to 100 m deep over the western Antarctic Peninsula, separates the shallow waters of the Bransfield Strait from the dense and relatively cold waters from the Weddell Sea shelves (Savidge & Amft 2009, Sangrà et al. 2011, 2017). In addition, Dense Shelf Water from the Weddell Sea reach the northern portion of the Gerlache Strait (Sangrà et al. 2011) and a Gerlache surface thermal front is marked by the influence of this water mass entering from the Bransfield Strait (e.g., Kerr et al. 2018b, da Cunha et al. 2018). Moreover, signs of a persistent surface thermal front were observed separating colder and fresher waters in the south from warmer and saltier waters in the north of the Gerlache Strait during the austral summers of 2015–2017 (Parra et al. 2020). The temporal changes and frontal systems of these water masses likely modify the distribution of heat, oxygen, and nutrient and, thus, influence the carbonate system, acidification processes, and primary production at NAP. However, this influence on the carbonate system has rarely been explored. For example, the hydrographic conditions

promoted by these fronts are prone to influence the vertical distribution of dissolved organic carbon (e.g., da Cunha et al. 2018) and probably impact regional sea-air CO₂ exchanges (Kerr et al. 2018c). Nevertheless, the vertical oceanic structure undergoes changes that cannot be easily monitored through traditional methods, mainly during the austral winter (Santini et al. 2013), making it a challenge to investigate changes in carbonate properties.

Furthermore, these frontal regions are prone to mesoscale activities, plus a stationary mesoscale eddy has been observed (Figure 1; Azaneu et al. 2017, Moffat & Meredith 2018). Though there is evidence that mesoscale eddies affect sea-air heat fluxes (e.g., Villas Bôas et al. 2015), there is no consensus on the expected behavior of cyclonic/anticyclonic eddies being either a sink or source of CO₂ to the atmosphere nor whether they enhance or reduce the sea-air CO₂ exchanges (Song et al. 2016, Jones et al. 2017, Moreau et al. 2017). The influence of mesoscale eddies on the biogeochemistry of oceans is not fully understood, although it is generally agreed that these structures will modify the biogeochemical environment (e.g., Ríos et al. 2003, Woosley et al. 2016, Moreau et al. 2017, Orselli et al. 2019a, b). Considering other ocean basins, studies indicate that Ekman and/or eddy-pumping mechanisms will affect surface CO₂ fluxes (Chen et al. 2007, Jones et al. 2017, Orselli et al. 2019a), C_{ant} penetration into the interior of oceans (Orselli et al. 2019b), nutrient availability and the distribution of carbonate system properties (Wang et al. 2013). This also leads to different conditions for phytoplankton growth (e.g., Carvalho et al. 2019). Recent studies observed the impacts of Southern Ocean eddies on iron and light availability for phytoplankton populations during summer and winter periods (Rohr et al. 2020a, b). The authors reported higher iron availability in anticyclones throughout the

year while during winter they observed poor light conditions due to the increased depth of the mixed layer. All these consequences are caused by the eddy-induced Ekman pump mechanism (Rohr et al. 2020a).

In addition, a stationary anticyclonic eddy, and other mesoscale features along NAP (Azaneu et al. 2017, Moffat & Meredith 2018), influence phytoplankton distribution and biomass (Rohr et al. 2020a, b). These eddies are formed between the Bransfield Front and the Peninsula front and trap warm water, enhance stratification, and upwell nutrients and iron, promoting ideal conditions for phytoplankton (Kahru et al. 2007). Additionally, anticyclonic eddies are being indicated as playing a significant role in the carbonate system. Such eddies have been observed in the Southern Ocean (Moreau et al. 2017) and in the South Atlantic Ocean, even at the sea surface, acting to increase sea-air CO₂ sink to the ocean interior (Orselli et al. 2019a) or through the water column, transferring C_{ant} to deeper layers (Orselli et al. 2019b).

Sea-air CO₂ fluxes along the northern Antarctic Peninsula

Seasonal and interannual variability of sea-air CO₂ fluxes

One of the biggest challenges to better understand the marine carbon cycle along NAP environments is ensuring a continuous and robust time series of biogeochemical variables. This is necessary because of the great temporal variability of carbonate system parameters. For instance, in the Gerlache Strait, temporal variability of summer FCO₂ oscillates between strong CO₂ sink (i.e., < -12 mmol m⁻² day⁻¹) and near-equilibrium conditions (i.e., sea-air CO₂ difference ≈ 0) at interannual scales (Monteiro et al. 2020a). From 1999 to 2017 there were two cycles, one with a 2-year periodicity and the

other with a 4-year periodicity, with the 2-year periodicity being stronger after 2012, which reveals an intensified strong summer CO₂ sink scenario for the region (Monteiro et al. 2020a). A robust 25-year time series, with similar summer FCO₂ oscillation and CO₂ sink intensification, has been studied south of NAP (Brown et al. 2019), revealing that the drivers of long-term FCO₂ variability are likely medium to large spatiotemporal events. Two of the main long-term drivers of FCO₂ variability along NAP are likely the previously characterized ENSO and SAM climate modes (see The influence of climate mode signals on the carbonate system). It has already been recognized that these climate modes can affect phytoplankton succession (e.g., Brown et al. 2019, Costa et al. 2020), and organic carbon distribution (e.g., Avelina et al. 2020), apart from the physical characterization of the ecosystem (e.g., wind-speed and direction, front positions, Circumpolar Deep Water intrusions). In fact, these events are linked to physical and biogeochemical processes in the Southern Ocean as a whole (Lovenduski et al. 2007, Hauck et al. 2013, Keppler & Landschützer 2019). However, there are still many uncertainties regarding FCO₂ along NAP in the future under conditions of positive SAM trends and intensified westerly winds and likely Circumpolar Deep Water upwelling.

Near-equilibrium scenarios of summer FCO₂ were associated with the intensification of Circumpolar Deep Water upwelling linked to positive SAM at NAP (Monteiro et al. 2020a). Since positive SAM is expected to persist in the coming years (Dinniman et al. 2012, Keppler & Landschützer 2019), the weakening of the summer CO₂ sink has already been hypothesized (Brown et al. 2019, Keppler & Landschützer 2019, Monteiro et al. 2020b). Moreover, the shift in dominant phytoplankton groups, from large diatoms to small flagellates, in the community

of primary producers (Mendes et al. 2013) may be an important driver of this weakening of the CO₂ sink (Brown et al. 2019, Costa et al. 2020). For example, this was observed in a particular condition in the Gerlache Strait in 2015, when the dominance of cryptophytes (Kerr et al. 2018c), which are less efficient for CO₂ uptake (Gao & Campbell 2014, Brown et al. 2019, Costa et al. 2020), led to an atypical release of CO₂ in the region during summer (Kerr et al. 2018c).

On the other hand, the increase in atmospheric and oceanic temperature (Siegert et al. 2019) and the prolongation of the sea ice-free period (Shepherd et al. 2018, Del Castillo et al. 2019), and hence prolonged phytoplankton growth (Del Castillo et al. 2019), may lead to an enriched intensification of the CO₂ sink along NAP. This has been identified as the most likely future scenario because months with a strong CO₂ sink have become more frequent since 2010, when the region started to act mainly as a weak annual CO₂ sink (Monteiro et al. 2020b). However, this behavior can be counteracted as the sea ice-free season is extended beyond the summer, releasing CO₂ that would otherwise remain in seawater isolated by sea-ice. Sea-ice dynamics promotes a shift in dominant biogeochemical factors from summer (lower *p*CO₂) to early winter (higher *p*CO₂) (Shetye et al. 2017). This reveals the sensitivity of sea-air CO₂ exchanges to these feedback mechanisms and the urgent need to broaden investigations for a coupled analysis of ocean-climate systems (Monteiro et al. 2020b). To understand such mechanisms, one needs to investigate the seasonal sea-ice driven CO₂ flux dynamics to assess the contributions of coastal regions of Antarctica to the global oceanic CO₂ budget.

The seasonal dynamics of FCO₂ in part of NAP is more sensitive to climate change than previously thought. This is because the estimated annual budget from 2002 to 2017 in

the Gerlache Strait was 1.24 ± 4.33 mmol CO₂ m⁻² day⁻¹, with high seasonal and interannual variability. In addition, since 2010, the region has been acting predominantly as a weak annual CO₂ sink after a period, between 2002 and 2009, of acting predominantly as an annual CO₂ source (Monteiro et al. 2020b). Although this study has broadened our understanding of the seasonal cycle of FCO₂ in NAP, it is relatively spatially limited. Efforts have been made to expand the spatial coverage of FCO₂ along NAP, however, these studies were limited to one year (Costa et al. 2020) and/or summer conditions (Ito et al. 2018). Importantly, some studies were conducted south of NAP (Legge et al. 2015, Jones et al. 2017, Brown et al. 2019), where the physical and biogeochemical characteristics are similar, although most of these were also spatiotemporally or seasonally limited. Despite sampling in different years, Legge et al. (2015), Jones et al. (2017) and Brown et al. (2019), noted that diatoms absorb more CO₂ than other phytoplankton groups because they reach greater biomass. These authors observed that changes in sea ice dynamics led to an increase in upper ocean stability. As a consequence, there will be an increase in phytoplanktonic biomass and a reduction in biological DIC, effected by an almost five-fold increase in the absorption of oceanic CO₂ in the summer. Therefore, it is necessary to broaden our understanding of the south of NAP to solidify knowledge for the other periods.

Although practically all physical and biogeochemical processes have some influence on seawater pCO₂ in summer (Monteiro et al. 2020a, b), the main driver of changes in this parameter is biological activity (Álvarez et al. 2002, Kerr et al. 2018c, Brown et al. 2019, Monteiro et al. 2020a, b). Due to the shallower and more stable mixed layer, the growth of phytoplankton in late spring decreases seawater pCO₂, leading

to a strong ocean CO₂ sink until late March. As the formation of sea ice has intensified since April, there is a deepening of the surface mixed layer coupled with the greater intensity of intrusions and episodic upwelling of Circumpolar Deep Water along NAP, leading to an increase in seawater pCO₂. These conditions, associated with greater wind speed intensity in winter, lead to an increase in ocean CO₂ release, the peak of which in winter occurs in August, together with maximum sea ice coverage (Monteiro et al. 2020b). Nevertheless, it is important to emphasize that more information for seasons other than summer (Figure 3) is necessary to endorse some points raised by recent studies. For example, sparse sampling of carbonate system parameters in winter is evident, leading to the need to estimate these parameters from other data, such as TA that is often estimated from salinity (Figure 4). Although the correlation among the parameters is generally very well defined in the summer (e.g., TA vs SSS; Hauri et al. 2015, Brown et al. 2019, Monteiro et al. 2020a, b), it is not clear whether this correlation is consistent throughout the year (see CO₂-carbonate system data). Therefore, future studies should shed light on how carbonate system parameters and physical properties correlate with each other throughout the seasons. In addition, increased observations for seasons other than summer will allow the construction of more accurate models and, consequently, improve knowledge of the seasonal cycle of CO₂ in the region of NAP (Ogundare et al. 2021). Hence, it is necessary to make new efforts to combine spatial and temporal scales with seasonal coverage to provide a more realistic scenario of the carbon cycle in NAP.

The intensity of FCO₂ in the coastal regions of Antarctica is strongly driven by wind speed (Sutton et al. 2021), which is highly variable. This has been reported as one of the main

sources of uncertainty in FCO_2 calculations for these regions (Sutton et al. 2021). The choice of using instantaneous, weekly, or monthly averages has not been clear or standardized in studies. Although this choice does not change the CO_2 source/sink behavior of the regions, the influence on FCO_2 intensity should not be tossed aside. Besides, the influence of sea ice cover during summer is neglected by several of these studies (e.g., Álvarez et al. 2002, Ito et al. 2018, Kerr et al. 2018c, Monteiro et al. 2020a, Costa et al. 2020). Although this is consistent among many studies, which facilitates their comparison, a recent study points out that FCO_2 can be overestimated by up to 30% in the summer if sea ice cover is not considered (Monteiro et al. 2020b). This weighting has also been applied to global FCO_2 climatologies (Roobaert et al. 2019), reinforcing its importance for regional studies. Indeed, coastal areas, such as those of NAP, are often disregarded from global FCO_2 climatologies, hindering a complete understanding of the behavior of the carbonate system.

The importance of coastal regions regarding sea-air CO_2 fluxes

Global FCO_2 climatologies have historically neglected coastal regions (e.g., Lenton et al. 2012, Takahashi et al. 2014), however, recent climatologies are making efforts to better understand their complexity (Roobaert et al. 2019). Although NAP has been the focus of most of these regional studies, as have some areas of Antarctica (e.g., Prydz Bay, Wang et al. 2020), our understanding of the carbon cycle, both at the surface and in the deep ocean, is still limited in this region. This is particularly true for the biogeochemical processes that influence FCO_2 over space and time (e.g., primary production, remineralization, calcification, CaCO_3 dissolution, N_2 fixation, denitrification, sea-air CO_2 exchange)

(Humphreys et al. 2018). Studies have shown the importance of coastal regions of Antarctica as strong CO_2 sinks during summer (Gibson & Trull 1999, Shadwick et al. 2013, DeJong & Dunbar 2017, Monteiro et al. 2020a, b). Thus, these regions are likely to uptake as much, or more, CO_2 than open ocean areas of the Southern Ocean in other seasons (DeJong & Dunbar 2017, Monteiro et al. 2020a), although such studies are almost exclusively limited to the summer period.

Considering coastal areas as strong CO_2 sinks, we are led to highlight the importance of the cross-shelf exchange that has already been indicated as a relevant process in the South Atlantic Ocean (Brazil, Carvalho-Borges et al. 2018, Argentinean Patagonia, Orselli et al. 2018). Therefore, it is necessary to broaden our understanding of both the coastal environment of NAP and the seasonal dynamics of the carbon cycle, which is exclusive to regional studies. Furthermore, it will be necessary to clarify the importance of these regions for the Southern Ocean CO_2 sink. As efforts are made towards these general aspects, specific questions will still be raised, such as: (i) What is the connection between strong CO_2 -sink coastal regions and adjacent open ocean areas? (ii) What is the importance of surface and subsurface circulation in this dynamic? (iii) How will changes in the properties of the carbonate system at sea surface impact FCO_2 ?

Another aspect raised by studies conducted at NAP refers to its particular location around 60°S – 65°S and the influence of the Antarctic Circumpolar Current, which leads to intense Circumpolar Deep Water intrusions (Moffat et al. 2009, Moffat & Meredith 2018). There is a region of annual neutral FCO_2 around 60°S , which is likely due to the upwelling of Circumpolar Deep Water during winter (Takahashi et al. 2012, Henley et al. 2020). However, most of these FCO_2 studies conducted at NAP (e.g., Álvarez et al.

2002, Ito et al. 2018, Kerr et al. 2018c, Monteiro et al. 2020a, b) are not linked to the vertical distribution of physical properties capable of precisely identifying signs of upwelling in the region. Therefore, future biogeochemical studies along NAP should face the challenge of coupling the signs of upwelling in time and space to empirically quantify their influence on regional FCO_2 . For instance, the influence of Circumpolar Deep Water on FCO_2 has been empirically demonstrated recently in Prydz Bay by a physical-biogeochemical study (Wang et al. 2020), even though the Antarctic Circumpolar Current is running away from the continent in the region. The influence of depth on $p\text{CO}_2$, and hence FCO_2 , in sheltered coastal areas of NAP has already been reported (Caetano et al. 2020). In shallower regions, vertical mixing leads to organic matter enrichment at the surface, which limits primary production and CO_2 uptake when coupled with the light attenuation (Caetano et al. 2020).

Phytoplankton influence on sea-air CO_2 fluxes

Biological activity acts as the dominant process in removing inorganic carbon from surface waters during summer along NAP (Ito et al. 2018, Costa et al. 2020). Moreover, a high signal of local ocean CO_2 absorption was associated with a diatom bloom during the late summer of 2016 in a vast area of NAP (Costa et al. 2020). Meanwhile, high seasonal and interannual variability was found in a coastal region of NAP, which acted as sink (source) of CO_2 during spring/summer (autumn/winter), with influences from both physical and biological processes (Monteiro et al. 2020b). However, as investigations occur mostly during summer, an understanding of the role of phytoplankton in CO_2 uptake throughout seasons is still missing.

In the short-term, sea surface warming and early sea-ice retreat have been associated

with an increased abundance of cryptophytes (Mendes et al. 2012, 2013, 2018a, b) and water column stability was identified as the main driver controlling both the biomass and composition of phytoplankton communities (Mendes et al. 2012, Höfer et al. 2019, Costa et al. 2020). In the long-term, the intensification of warming conditions is expected to favor smaller phytoplankton cells (i.e., *Phaeocystis antarctica*, Petrou et al. 2016). The establishment of shallow water-column stratification favors the shift from diatoms to cryptophytes (Moreau et al. 2010) due to their tolerance to high light levels, thriving under confined stratified upper layers (Mendes et al. 2018a, b). As diatoms achieve significantly higher biomass and oceanic CO_2 uptake than cryptophytes (Brown et al. 2019), there will be implications for local FCO_2 of the coastal waters of NAP (Kerr et al. 2018c, Costa et al. 2020). Although the scientific community has expended efforts to unravel the role of phytoplankton in a warmer ocean, there are still many knowledge gaps that need to be filled towards a complete understanding of how phytoplankton communities will change over the years, especially due to ongoing anthropogenic carbon emissions and ocean acidification processes, and influence CO_2 uptake.

Anthropogenic carbon inventory and ocean acidification status along NAP environments

Anthropogenically-driven CO_2 uptake by oceans leads to intense changes in the conditions of the carbonate system. A change in pH of 0.1 corresponds to an increase of 30% in seawater $[\text{H}^+]$ (The Royal Society 2005). Keeping this in mind, we point out that Global Oceans have already absorbed ~25–30% of C_{ant} (e.g., Khatiwala et al. 2009, Watson et al. 2020), ~40% of which was absorbed by the Southern Ocean (e.g., Khatiwala et al. 2009, Frölicher et al. 2015, Gruber et al. 2019). This fact makes the Southern Ocean

the most important area of C_{ant} uptake in the world (Tanhua et al. 2016).

To this day, it remains a challenge to separate the C_{ant} signal from natural variability of DIC due to biogeochemical sources and sinks (Hall et al. 2002). The first to attempt to do so was Gruber et al. (1996), who created a method called ΔC^* , which was tested on North Atlantic waters and is widely applied. One of the assumptions of the method is that the stoichiometric ratios $C:O_2$ and $N:O_2$ are constant, which can lead to bias and large uncertainties (Hall et al. 2002, 2004, Matsumoto & Gruber 2005). As for ΔC^* , other approaches (e.g., MIX method - Goyet et al. 1999, TrOCA method - Touratier & Goyet 2004) also have various assumptions that can lead to bias. These methods can use either DIC measurements or tracers in their equations, such as $\Delta^{14}C$, which was used in the development of the TrOCA method. Despite the number of methods and studies developed, there is still no consensus on which calculation returns the most correct results.

C_{ant} inventory

Due to its cold and less salty water, together with mixing processes, Antarctic Surface Water absorbs and stores large amounts of C_{ant} , which is distributed by regional circulation to other NAP regions (Khatiwala et al. 2009, Pardo et al. 2014, van Heuven et al. 2014, Kerr et al. 2018d). In the Gerlache Strait, intrusion of C_{ant} -rich waters in layers deeper than 100 m comes from continental shelf waters formed in the Weddell Sea, especially the high salinity variety of Dense Shelf Water (Kerr et al. 2018d). These waters have recently been exposed to the atmosphere in a region highly susceptible to climate changes, thus inducing carbon uptake. Moreover, the relatively rapid rate at which this Dense Shelf Water enters the Bransfield Strait may shed some light on the interannual changes that the

Gerlache Strait will experience from this input (van Heuven et al. 2014, Dotto et al. 2016, Kerr et al. 2018d, Damini et al. 2022).

For instance, Kerr et al. (2018d) reported that waters deeper than 100 m in the Gerlache Strait store $21.2 \pm 16.7 \mu\text{mol kg}^{-1}$ of C_{ant} , with consequent decreases in pH, calcite and aragonite saturation states ($\Omega_{\text{Ca}}, \Omega_{\text{Ar}}$) of -0.064 ± 0.050 , -0.24 ± 0.19 and -0.15 ± 0.12 , respectively. Lencina-Avila et al. (2018) reported C_{ant} contents ranging from 50 to 150 (depending on the estimation method), with an average of $110.1 \pm 25.4 \mu\text{mol kg}^{-1}$ within the surface mixed layer of the Gerlache Strait in 2015. These authors reported that undersaturation conditions of α_{Ar} appear only below the surface mixed layer, mainly due to the buffering capacity favored by TA. However, episodic undersaturation events may occur within the surface mixed layer (Lencina-Avila et al. 2018). Overall, a few authors have reported C_{ant} in the NAP region and vicinities by different methods since the 1980s, with accumulation averages ranging from 20 to $40 \mu\text{mol kg}^{-1}$ below de mixed layer (e.g., Anderson et al. 1991, Sandrini et al. 2007, Pardo et al. 2014).

Large temporal and spatial investigations are extremely important to visualize C_{ant} uptake trends. This is justified because C_{ant} uptake affects the buffering capacity of seawater by altering the other carbonate system parameters (pH, $\Omega_{\text{Ca}}, \Omega_{\text{Ar}}$), which have implications for the ecosystem as a whole (Sabine et al. 2004, Fabry et al. 2009, Kerr et al. 2018c, d). However, this type of study is problematic when it comes to NAP due to the difficulty with sampling throughout the year (especially in winter) in coastal areas and at a high-frequency (Hauri et al. 2015, Kapsemberg et al. 2015, Kerr et al. 2018d, Henley et al. 2019).

Although *in situ* studies are snapshots of a highly variable environment, earlier results highlight the biogeochemical sensitivity of this environment and the intricate consequences that may result. To overcome this sampling difficulty

and help separate natural biogeochemistry variability from that which is anthropogenically-driven, studies using reconstructed/ modeled data are posing as a reliable solution (e.g., Caldeira & Duffy 2000, Orr et al. 2001, Ito et al. 2010, Hauri et al. 2015, Brown et al. 2019, Monteiro et al. 2020a, b).

The influence of the residence time of surface and subsurface waters in the carbonate system is also poorly understood. As far as we know, the residence time of water masses in NAP and the C_{ant} accumulation rate are increasing (Hauck et al. 2013). Regarding NAP, we are not aware of studies considering CO_2 accumulation in the Bransfield and Gerlache Straits, or even estimates of C_{ant} export to the global ocean. Results not yet published by the GOAL group indicate that the central basin of the Bransfield Strait potentially accumulates more C_{ant} than the eastern basin, which is likely related to their rate of deep water renewal (Torres-Lasso 2019).

Effects of ocean acidification on marine organisms and NAP ecosystems

Among the impacts caused by the rapid uptake of C_{ant} by Antarctic Surface Water, ocean acidification is one of great concern (Henley et al. 2019, 2020). The natural CO_2 -rich Southern Ocean waters reflect a low buffer capacity and carbonate saturation states, which, combined with a lowering pH driven by the growing CO_2 uptake, is changing ocean chemistry. Thus, the Southern Ocean is expected to be one of the first places on Earth to display the consequences of ocean acidification, which is expected to occur in the next few decades (Sabine et al. 2004, Feely et al. 2009, Doney et al. 2009, Kapsemberg et al. 2015, Monteiro et al. 2020b).

Besides the absorption of CO_2 by surface waters, the upwelling and advection of CO_2 -rich waters (natural or C_{ant} -affected) is another factor accelerating the shoaling of the carbonate

(calcite and aragonite) saturation states horizon – in other words, the depth where Ω_{Ca} and Ω_{Ar} are lower than 1, and which leads to the dissolution of marine calcium carbonate (CaCO_3), directly affecting many calcifying organisms (Gutt et al. 2015, Lencina-Avila et al. 2018, Kapsemberg et al. 2015). Hauri et al. (2015) points out that an ongoing freshening of southern waters, due to melting of ice shelves, induced by global warming, causes a dilution of carbonate (CO_3^{2-}) ions, which in turn decreases Ω_{Ar} . The undersaturation of Ω_{Ar} is expected to play an important role in the Southern Ocean, with model simulations suggesting that ~30% of surface Southern Ocean waters will be impacted by 2060 (Gutt et al. 2015, Hauri et al. 2015).

NAP includes regions of high primary production (e.g., Mendes et al. 2012, 2013, 2018a, b), like the Gerlache Strait, which supports feeding grounds for a large ecosystem sustaining different trophic levels (e.g., Secchi et al. 2011, Cavan et al. 2019, Henley et al. 2019, 2020). Ocean acidification, driven by lowering pH or shoaling $\Omega_{\text{Ca}}/\Omega_{\text{Ar}}$ depth horizons, and powered by other issues of climate change, like the growing input of glacial meltwater and global warming, alters the environment in which phytoplankton and zooplankton grow, which in its turn may modify the food chain patterns of an intricate and delicate environment. Since the consequences of such changes are still unclear, the abundance of these organisms may fall, leading to situations of stress in the ecosystem (Bopp et al. 2013, Kerr et al. 2018c, d, Henley et al. 2020).

Even though ocean acidification has been known to be a problem for a relatively long time (Doney et al. 2009, 2020), the scientific community is still trying to fully understand its consequences on marine biota, ecosystems, and climate. We know that some organisms will struggle to survive in such different environments, but whether they can adapt and

recover remains a question. If so, how long will it take for the community, in all its complexity, to be restored? How long can the ecosystem sustain such changes? What are the tolerance limits of organisms? These questions can only be answered with large temporally and spatially scaled studies and with a great deal of controlled experiments, taking into consideration natural seasonal environmental fluctuations, which is proving to be hard to accomplish in such a challenging environment.

CONCLUSIONS

Here we addressed the state-of-the-art of CO₂-system research on NAP. We presented the seasonal dynamics of pCO₂ and TA along NAP through the analysis of SOCAT version 2020 (Bakker et al. 2016) and the seasonal gridded dataset for NAP from GOAL (Dotto et al. 2021). We indicate a disproportional sampling throughout the year, which prevents comprehension of the seasonal carbon cycle in this region. We discussed knowledge gaps that are currently being indicated in studies regarding the sea-air CO₂ exchange processes, as well as C_{ant} and its consequences for organisms and ecosystems, along with the main physical processes that act in NAP environments. Our main remarks regarding current knowledge and suggestions for future investigations are summarized in Figure 5.

Firstly, we indicate the sensitivity of FCO₂ considering sea-ice dynamics. If the sea ice-free season extends beyond summer, the CO₂ that would otherwise remain in seawater will be released into the atmosphere, which could weaken the annual CO₂ sink along NAP. FCO₂ can be overestimated by up to 30% in the summer if sea ice cover is not considered, so the mechanisms acting on it need to be the focus of coupled analyses of ocean-climate

systems. Regarding seasonality dependence, we presented evidence that summer corresponds to a strong CO₂ sink in coastal areas, with uptake in coastal areas at magnitudes equal to or greater than that in the open ocean. Therefore, we also mention cross-shelf exchange as an important process to be investigated. Additionally, the influence of mixing processes on CO₂ outgassing should be examined. Still linked to seasonality, biological activity plays a significant role in CO₂ drawdown. However, possible changes to the phytoplankton community and its effects on CO₂ uptake seems to be a research gap for the scientific community to address. Some questions raised are related adaptations of organisms to the forthcoming changes to communities, and even related to ecosystems, forced by ocean acidification and/or temperature modifications. Thus, large temporal investigations and complex experiments are necessary to determine natural environment fluctuations on a seasonal basis. This determination is also important for differentiating natural carbonate system variability from anthropogenically-driven changes. Considering C_{ant}, we highlight the importance of developing more studies regarding uptake rate, accumulation, and export to global oceans.

Climatic modes, such as ENSO and SAM, are indicated as playing a role in the carbonate system, however, studies suggest contradictory influences. This ambiguity may be due to the different responses they can lead to in each region according to the geographic position of sampling. These modes also influence Circumpolar Deep Water intrusions and changes in sea ice coverage around NAP, whose impact on the carbonate system remains unquantified. Modelling studies indicate more CO₂ uptake and associated ocean acidification in the region in the case of simultaneous positive ENSO and SAM. Stationary eddies have been observed along

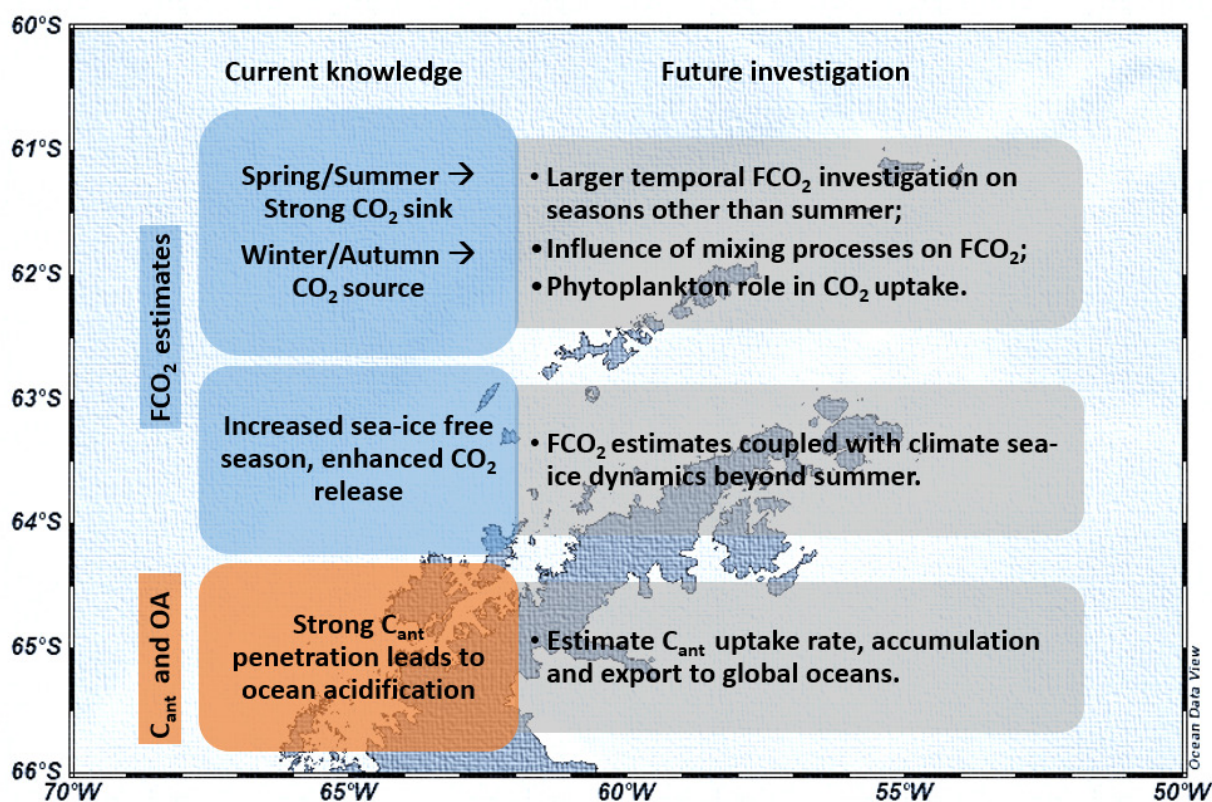


Figure 5. Summary of the main remarks regarding current knowledge and suggestions for future investigations explored in this study of the northern Antarctic Peninsula. The topics explored here regard sea-air CO₂ net fluxes (FCO₂), anthropogenic carbon (C_{ant}), and ocean acidification (OA).

NAP and their role in carbonate system changes should be looked at according to indications of studies of the contributions of these features to biogeochemistry, phytoplankton growth, sea-air heat fluxes, FCO₂ and C_{ant} transport. Additionally, the role that frontal systems play with regard to the carbonate system also needs to be clarified. Thus, it is important to reinforce the sensitivity of NAP to climate change because the Southern Ocean is already the region most affected by C_{ant} penetration, making it particularly prone to the consequences of ocean acidification.

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