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Physical and biological processes that control the distributions of carbonate chemistry across the ACC domains and the marginal ice zone in the Southern Atlantic sector of the Southern Ocean.

By

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26/09/2024

Signed

Date

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DEDICATION

This thesis is dedicated to my late mother (Nombini Maqungo), my daughter Lukhanyo Luminjalo Dyoyi and my entire family.

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Abbreviations

μΜ	Micromolar	
AABW	Antarctic Bottom Water	
AAIW	Antarctic Intermediate Water	
AASW	Antarctic Surface Water	
ACC	Antarctic Circumpolar Current	
ANT	Antarctic	
AOU	Apparent Oxygen Utilization	
BCP	Biological Carbon Pump	
CA	Carbonate alkalinity	
CaCO ₃	Calcium carbonate	
Chl-a	Chlorophyll-a	
CO ₂	Carbon dioxide	
CRM	Certified Reference Material	
DIC	Dissolved inorganic carbon	
DO	Dissolved oxygen	
DOC	Dissolved organic carbon	
HCO3 ⁻	Bicarbonate	
H ₂ CO ₃	Carbonic acid	
HNLC	High Nutrient Low Chlorophyll	
LCDW	Lower Circumpolar Deep Water	
MIZ	Marginal Ice Zone	
MOC	Meridional Overturning circulation	

NADW	North Atlantic Bottom Water
NO ₃	Nitrate
pCO ₂	Partial pressure of carbon dioxide
PF	Polar Front
PgC	Petagram of carbon
рН	Potential of Hydrogen
PO ₄	Phosphate
Ppm	Parts per million
sACCF	Southern Antarctic Circumpolar Current Front
SAF	Subantarctic Front
SAMW	Subantarctic Mode Water
SANT	Subantarctic
SBDdy	Southern Boundary
SCALE	Southern oCean seAsonaL Experiment
SiO ₄	Silicate
SO	Southern Ocean
SOCCOM	Southern Ocean Carbon and Climate Observations and Modelling
SP	Solubility Pump
SSS	Sea Surface Salinity
SST	Sea Surface Temperature
STF	Subtropical Front
STSW	Subtropical Surface Water
STZ	Subtropical zone

ТА	Total alkalinity
UCDW	Upper Circumpolar Deep Water
VINDTA	Versatile INstrument for Determination of Total Alkalinity

Abstract

The Southern Ocean plays an important role in global climate systems as a major sink of atmospheric carbon dioxide through the biological and physical pumps that are responsible for absorbing atmospheric carbon dioxide, storing heat, storing freshwater (sea ice) and transporting carbon to the deep ocean. The Southern Ocean is the least sampled ocean region, due to its remote location, cold, windy, and rough weather conditions. The number of available in-situ carbonate chemistry observations are seasonally biased because they are largely done in the summer season, and few have been reported for the winter to spring period. This has hampered our understanding of the full seasonal biogeochemical cycle of carbonate chemistry in this important ocean region. Furthermore, it is not well understood how models respond to these gaps due to the lack of in-situ observations. To close these gaps and improve our understanding of the spatial and temporal variability of the carbonate system in the Southern Ocean, seawater samples for carbonate chemistry (Dissolved Inorganic Carbons and Total Alkalinity) and macronutrients were collected along the GEOTRACES transect (GT) and the marginal ice zone during the Southern oCean seAsonaL Experiment (SCALE) cruise in October 2019.

In this thesis, the distributions of the carbonate system variables and the associated physical and biological processes that control its distributions across the different Antarctic Circumpolar Current domains (Subtropical, Subantarctic and Antarctic domains) are described and presented. The dataset collected was grouped into two transects, namely the open ocean GEOTRACES transect and the Marginal Ice Zones and used to characterise the distribution of dissolved inorganic carbon and total alkalinity in the south Atlantic sector of the Southern Ocean. The water column distributions of dissolved inorganic carbon and TA concentrations, along both transects, showed low concentrations at the surface waters that increased with depth. The northward decrease in DIC in the AAIW indicates the northward transport of anthropogenic CO₂ captured in the Southern Ocean. The Subtropical domain and the Subantarctic domain had the lowest Dissolved Inorganic Carbon concentration with slightly higher Total Alkalinity concentrations at the surface compared to the Antarctic domain. The intermediate waters (Subtropical domain: 748 m to 1251 m; Subantarctic domain: 6 m to 748 m) had slightly higher Dissolved Inorganic Carbon concentrations and lower Total Alkalinity concentrations while the deeper waters had high Dissolved Inorganic Carbon and Total Alkalinity. The main processes that controlled the carbonate chemistry across these domains were different. The dissolution of CaCO₃ minerals dominated the Antarctic and Subantarctic

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domains whereas the processes of CO₂ release by the ocean, photosynthesis and to a lesser extent, the dissolution of CaCO₃ dominated the Subtropical domain.

1.1: Motivation

Atmospheric carbon dioxide (CO₂) concentrations have increased since the start of the industrial revolution due to human activities, such as the burning of fossil fuels and deforestation (Sabine et al., 2004). The ocean covers over 70% of our planet (Williams et al., 2018), and the ocean's uptake of atmospheric CO₂ is due to it having a relatively high buffer capacity (regulating alkalinity to ensure the ability of the ocean to absorb CO ₂ is not compromised) (de Carvalho-Borges et al., 2018). Even though the Southern Ocean makes up approximately 30% of the world's surface south of 30°S, it is responsible for sinking over 43% of the CO₂ that originates from human sources (Williams et al., 2024).

The Southern Ocean (SO) plays an important role in global climate systems as a major sink for atmospheric CO₂ through the biological and physical pumps that are responsible for absorbing atmospheric CO₂, storing heat, and transporting carbon to the deep ocean (Jones et al., 2010). Climate change is already having an impact on the SO. Temperature is rising, ocean fronts are migrating southward, and sea ice cover is changing (Constable et al., 2014). As the greatest anomaly in historical records, the declining sea ice cover recorded since 2016 is just one example of how recent changes in Antarctic Sea ice are a significant indicator of warming (Meehl et al., 2019). The Southern Ocean and the Antarctic are critical to the global climate, hence understanding the changes they are experiencing is of urgent importance.

In 2019 on the 12th of October to the 19th of November, a cruise was undertaken from the southwest coast of South Africa to the SO. The Southern oCean seAsonaL Experiment (SCALE) spring cruise was aimed at studying the different oceanographic aspects of the SO, including the carbonate chemistry and CO₂ exchange dynamics. SCALE is a new interdisciplinary experiment in the south-east Atlantic sector of the SO that extends seasonal to decadal time scales. It contributes both long-term and experimental observations towards a greater understanding of the role of fine-scale dynamics in shaping the phasing and magnitude of the Southern Ocean seasonal cycle through novel integrated ship and robotics experiments. Most studies that focused on the carbonate chemistry of the SO were conducted in summer and a few in winter (Williams, et al., 2018; González-Dávila et al., 2011), with little to no studies focusing on the spring season, meaning that the full understanding of the seasonal cycle of the carbonate chemistry, which is important for model parameterization to predict future climate impact in this ocean region is lacking.

1.2: Problem Identification

The partial pressure of atmospheric CO₂ (pCO₂) is expected to rise from its current value of roughly 400 ppm (Friedlingstein et al., 2020) to about 800 ppm by 2100 (Ciais et al., 2013) as a result of continuous anthropogenic CO₂ emission. This has resulted in a drop of 0.1 in ocean pH (Oppenheimer et al., 2019). Ocean acidification, often referred to as OA, is known to have a variety of consequences on marine ecosystems, including altering the composition of phytoplankton communities and causing physiological and evolutionary alterations in some species such as the shelled pteropods (Hoppe et al., 2013; Lohbeck et al., 2012). This will have an impact on oxygen generation, interactions between grazers and viruses at the trophic level, and the strength and effectiveness of the biological carbon pump (BCP). By removing 3 PgC from surface waters south of 30°S each year (Schlitzer, 2002) and controlling the transport of nutrients to low-latitude ecosystems (Sarmiento et al., 2004), the SO BCP significantly contributes to the global carbon flux.

According to climate model projections, the SO is especially vulnerable to OA, with some ecological effects already being seen in pteropods and other major effects on calcifying species (Bednarsek et al., 2016; Sasse et al., 2015). The OA (caused by the increasing intake of anthropogenic CO₂) would affect the physiology of marine photoautotrophs and the chemistry of marine carbonates, with repercussions for the biogeochemical cycling of essential nutrients and biological carbon export. According to future climate change predictions, the SO's pH will likely decline, but there will also likely be concurrent increases in warmth and a reduction in upwelled nutrients (Orr et al., 2005). A more comprehensive understanding of the ecosystem-level response to OA with accompanying changes in deep ocean carbonate chemistry reserves will result from understanding the potential feedback between OA and its effects on marine life e.g., creating conditions that limit availability of minerals used to build shells and skeletons for marine shelled organisms.

Due to its isolation and severe weather, the SO has historically been insufficiently sampled (Rintoul et al., 2012). Additionally, satellite data is not available in this area during austral winter in the high southern latitudes due to high cloud cover and darkness (Pope et al., 2017). The amount of in-situ carbonate chemistry observations that are currently available (DIC, pCO₂, pH, and Alkalinity) is seasonally skewed because none have been reported from winter to spring. Machine learning techniques help fill in some of these sample gaps. Due to a dearth of in-situ data, it is unclear how model uncertainties react to these gaps.

Seawater samples for carbonate chemistry (i.e., DIC and Total Alkalinity) and macronutrient measurements were collected along the GEOTRACES transect and the marginal ice zone (MIZ) during the SCALE cruise in the spring of 2019. This was conducted to fill the gaps and

enhance our understanding of the characteristics of the spatial and temporal variability of the carbonate system in the SO. From this study, the distribution of the carbonate system characteristics throughout the Antarctic Circumpolar Current (ACC) fronts and MIZ in the south Atlantic sector of the SO are described, together with the corresponding physical and biological factors.

1.3: Aims and Objectives

The aims of this study were:

1. to characterize the water column profiles of carbonate chemistry variables (DIC and TA) across different ACC domains and the marginal ice zone in the SO and address the spring-time observational gaps.

2. to quantify the relationship between the carbonate chemistry variables and other environmental variables such as the concentrations of nitrate, nitrite, phosphate and silicate, temperature, salinity, density of seawater, oxygen concentration, apparent oxygen utilization and chlorophyll-*a* concentration as a proxy for microalgae biomass.

3. to quantify bio-physico-chemical processes that control the distributions of DIC and TA across different domains and the marginal ice zone.

2.1: Southern Ocean (SO)

Given the lack of physical barriers limiting its flow and the powerful winds that sweep over its surface, the Southern Ocean (SO), which encircles the Antarctic continent south of around 50°S, is a unique oceanographic region. The Antarctic Circumpolar Current (ACC), which moves eastward close to the Polar Front (PF) without being blocked by any continents, is a distinctive characteristic of this area (Southern Ocean) (Figure 2.1). One of the strongest current systems on Earth, the SO is also characterized on a large scale by highly slanted isopycnals (lines of constant density of seawater) that are shallow to the south (Ansorge et al., 2005). The Atlantic, Indian, and Pacific Oceans are all included in the current system. The mean field in the SO is significantly altered by fluctuations on multiple timescales, making it a crucial location for both carbon uptake and outgassing.



Figure 2.1: Southern Ocean mean air-sea carbon fluxes from 1982 through 2016 (Blue: carbon uptake; red: outgassing) (Figure taken from Keppler, 2020 without modification)

The carbon uptake in the SO is impacted by various, frequently conflicting mechanisms. According to Lovenduski et al., (2015), the ACC's northward Ekman movement causes a divergence in the surface waters, which causes old, carbon-rich water to rise to the surface and cause outgassing nearby. Poleward-flowing warm waters that are mixing with cold subpolar waters in the area north of the ACC are under-saturated due to cooling, which enables carbon uptake. After that, this water is moved northward and subducted north of the Subtropical Front (STF) (Takahashi et al., 2002). Additionally, near the Antarctic coast, saltwater that has frozen generates the chilly, salty Antarctic Bottom Water (AABW) by brine rejection during sea-ice development (Talley et al., 2011). DIC is transported downward as this dense water mass descends as it sinks because it becomes less carbon-saturated as it cools (Figure 2.2).



Figure 2.2: Schematic of simplified mean circulation of carbon fluxes in the SO (Figure taken from Keppler, 2020 without any modification)

The SO is central in reducing global warming. However, the uptake of atmospheric CO ² brings about changes in the carbonate chemistry of seawater. As the ocean continues to absorb CO² from the atmosphere, it is important to understand the processes responsible for the CO² uptake including the distribution and changes in the carbonate system of the water column.

2.1.1 : Global importance of the Southern Ocean

The impact/importance of the SO in the Global climate system is scaled by its uptake of 43% \pm 3% of the total ocean uptake of CO₂ and 75% \pm 22% of the excess heat generated by anthropogenic CO₂ (Frölicher et al., 2015), and approximately 30% of primary productivity that influences the Biological Carbon Pump (BCP) (Sigman and Hain, 2012), making it disproportionately more important when it comes to buffering the impact of climate change. The SO was a net carbon supply to the atmosphere in pre-industrial times because the outgassing and upwelling regions in the SO predominated over carbon uptake (Gruber et al., 2009). However, the mean concentration gradient between the ocean and the atmosphere has shifted due to anthropogenic disruption of the carbon cycle, leading to net carbon uptake. The SO basin has changed from a pre-industrial net carbon source to a post-industrial net carbon sink.

Most of the deep ocean water in the world is from the SO, which also acts as its principal return pathway to the surface (via Meridional Overturning Circulation; MOC) (Toggweiler and Samuels, 1995; Marshall and Speer, 2012). Large volumes of deep water are brought to the surface of the ocean by upwelling in the open channel that circles the Antarctic continent due to a strongly divergent wind-driven flow. A portion of this deep water is heated and freshened near the top before being transferred northward, where it sinks into the ocean's depths (see Figure 2.3). The remaining upwelling waters move southward and are cooled and brinerejected into very dense Antarctic Bottom Water. The global heat, nutrient, and carbon balances are significantly impacted by the drawing up of deep waters and their subsequent transfer into the interior of the ocean. Because it is so cold, the upwelled water absorbs a lot of extra heat from the environment (Manabe et al., 1991). Since the upwelled water has not been in contact with the atmosphere for decades or even centuries depending on the depth in which they upwell from, it can also absorb a high quantity of anthropogenic CO₂ (Frey, 2018; Khatiwala et al., 2009). Additionally, the SO provides most of the ocean's biological production with nutrients that fertilize it (Sarmiento et al., 2004). The nutrients that have accumulated in the deep ocean over centuries because of the decomposition of organic matter are abundant in the upwelled water (Figure 2.3).

Reports of recent and expected changes have caused grave concern because of the SO's crucial role in the global climate system. The following changes have been noticed in recent decades: i) a faster and deeper subsurface warming than the average for the entire planet (Thompson et al., 2011); (ii) a faster and deeper SO overturning than the average for the entire planet (possibly related to a poleward intensification of the westerly winds due to rising greenhouse gas concentrations and polar stratospheric ozone depletion) (Gille, 2002); (ii)

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significant Antarctic ice mass loss (Rignot et al., 2008), sea ice melting, and surface water flux increase; (iii) a large-scale freshening of the surface ocean (Böning et al., 2008); and (iv) warming, freshening, and a slowdown in the formation of Antarctic Bottom Water (Purkey and Johnson, 2012), which may have contributed to the recent slowdown in the rise in global surface temperature (Meehl et al., 2011). In the following section, I will focus on the physical and biological processes/mechanisms dominating the air-sea carbon exchange in this dynamic ocean region.



Figure 2.3: Southern Ocean global importance (Figure taken from Meredith, 2019 without any modification)

2.1.2 : Air-sea CO₂ exchange in the Southern Ocean

The CO₂ flux bctwcc \rightarrow aií a \rightarrow d sca i \rightarrow the SO is driven by processes such as: the solubility pump (SP), the soft tissue pump and biological carbon pump (BCP) (Volk and Hoffert, 1985). In the following subsections we will discuss these processes in detail.

2.1.2.1 : The solubility pump

The solubility pump (SP) is supported by the ocean's thermohaline circulation, which involves deep-water formation at high latitudes and the subsequent transfer of surface CO₂ to depth in these waters, as well as the solubility of CO₂ in seawater, with more CO₂ dissolving at colder temperatures (Figure 2.4). It consists of subduction of DIC enriched, cold water and the abduction of the preformed DIC back to the surface. In addition, photosynthesis in the surface ocean converts DIC and nutrients into organic and inorganic particles. CO2 is easily exchanged between the two reservoirs because of its high solubility properties which are influenced by pH and temperature (Reid et al., 2009; Primeau et al., 2013). The SP (Figure 2.4) is associated with CO₂ export, using cooled surface waters, into the ocean interior. The high latitude cold waters favourably allow for CO₂ dissolution, by increasing the gas's solubility and density, thus facilitating uptake from the atmosphere (Bopp et al., 2015). Upon interaction with seawater, CO₂ immediately reacts to form carbonic acid, this carbonic acid (H₂CO₃) dissociates into bicarbonate (HCO⁻³), which further dissociates into H⁺ ions and carbonate ions (CO₃²⁻). The sum of CO_2 (aq), HCO⁻³ and CO_3^{2-1} is referred to as dissolved inorganic carbon (DIC) and, as the cold dense waters sink, there is isopycnic transport of DIC to the deep ocean. On the surface, due to the vertical gradient, there is more uptake from the atmosphere, which is driven by heat, wind, and freshwater fluxes (Reid et al., 2009). The SP accounts for roughly 40% of the world's surface to depth DIC gradient (Riebesell et al., 2009; Toggweiler et al., 2003). The other 60% of the surface-to-depth DIC gradient is accounted for by the BCP (Toggweiler et al., 2003).

According to Lenton et al., (2013), the SP's contribution to CO₂ uptake varies seasonally and regionally in the SO. According to Mongwe et al., (2018), the winter CO₂ uptake in the SAZ is primarily driven by low sea-surface temperatures, while the summer is marked by a minor CO₂ outgassing as a result of higher temperatures. In contrast, CO₂ outgassing predominates most of the year south of the PF due to the upwelling of deep waters rich in DIC (Mongwe et al., 2018). However, the BCP's action overrides the SP's, and it is the interaction of the two pumps that results in the yearly cycle of air-sea CO₂ exchange in the SO.



Figure 2.4: Schematic diagram of the solubility pump (Figure taken from Meredith, 2019 without any modification)

2.1.2.2 : The biological carbon pump (BCP)

The BCP is dependent on two processes: primary production and biocalcification. Both significantly influence the distribution of surface CO₂ fluxes by affecting DIC and TA.

a) Primary production

As seawater absorbs atmospheric CO₂, the CO₂ dissolves and forms carbonic acid in the surface ocean water. Hydrogen and bicarbonate ions are produced when the carbonic acid dissociates. Bicarbonate ions are taken up from seawater by phytoplankton and other microorganisms. Because of photosynthesis, they use the bicarbonate ions to build organic compounds and release oxygen. Some organisms use the produced organic matter for energy production, through respiration, leading to the release of DIC (Figure 2.5). Alternatively, the organic matter is exported from the surface of the ocean to the deep waters as sinking particles i.e., detrital matter or faecal pellets which is the decomposed product of larger marine organisms that have consumed smaller zooplankton or phytoplankton (Bopp et al., 2015). The sinking particles result in the net downward transfer of the organic matter to the deep ocean, in a process referred to as the "soft tissue pump". Additionally, the active export pump governed by zooplankton vertical migration via zooplankton grazing helps in the downward

transfer of organic matter (Figure 2.5). A small fraction of about 0.05 Pg C yr⁻¹ organic carbon is sequestered into the seafloor and the majority, 10 Pg C yr⁻¹, is transported into the deep ocean (Bopp et al., 2015).

This biologically sequestered carbon that ends up deep sea contributes to the Global Ocean CO₂ uptake. At the deep ocean, remineralisation will occur to increase DIC and release nutrients, and during upwelling, surface waters are replenished with nutrient rich waters and DIC from the ocean interior (Reid et al., 2009).



Figure 2.5: Schematic diagram of the air-sea CO_2 exchange pumps: the biological carbon pump (Daniels, 2015)

b) Biocalcification

The precipitation of calcium carbonate (CaCO₃), either in the form of calcite or aragonite for shell formation by marine species, affects atmospheric CO_2 in two ways. Firstly, through the carbonate counter pump: CaCO₃ is exported from the surface waters to the deep oceans,

creating an alkalinity gradient (decreased at the surface) that increases surface partial pressure of CO_2 (p CO_2) (Daniels, 2015). This increase in p CO_2 is analogous to the decrease in p CO_2 driven by the BCP, hence the counter pump term (Daniels, 2015). In the deep ocean, dissolution of CaCO₃ occurs to increase DIC and alkalinity through the release of CO_3^{2-} (Daniels, 2015). Secondly, roughly 25% of CaCO₃ does not undergo dissolution but rather gets buried, thus sequestering carbon (Daniels, 2015). Therefore, all three pumps contribute to the observed DIC gradient and distribution across the water column.

Global biogeochemical cycles depend heavily on the enormous and dynamic marine reservoir of carbon, which contains 4 x 10^{19} g of mass distributed unevenly among dissolved and particulate elements with different redox states (Takahashi et al., 2009). The two main pools are dissolved inorganic carbon (DIC = $[H_2CO_3] + [HCO_3] + [CO_3^{2-1}]$) and the less oxidized pool of dissolved organic carbon (DOC), which is mostly uncharacterized. Many biological processes result in and sustain a chemical imbalance between DIC and organic matter. The oceanic carbon cycle is defined as the reversible, frequently biologically mediated interactions between the dissolved and particulate carbon pools in the sea (Takahashi et al., 2009).

Through the process of photosynthesis, oxidized DIC is mostly converted to reduced organic matter (dissolved and particulate pools) in the euphotic zone of the world ocean. The source of reduced carbon and energy needed to support sub-euphotic zone metabolic processes ultimately comes from the upper ocean and is delivered down through advection and diffusion of dissolved organic matter, gravitational settling of particulate matter, and vertical migrations of pelagic organisms and phytoplankton. The relative contributions of each of these individual processes, commonly referred to as the "biological pump," may be predicted to fluctuate with changes in habitat or with water depth for a particular habitat as each of these processes is governed by a different set of environmental conditions (Takahashi et al., 2009).

The distinction between three biological pump components has been made, each of which represents a distinct group of ecological processes:

Rotating pump

The method by which certain organisms, such as fish and zooplankton, actively move carbon from the surface to the deep ocean through their vertical migrations is referred to as the "biological conveyor belt" or "rotating pump." By feeding on phytoplankton and other surfacedwelling organic compounds, such organisms take up carbon. They essentially transport this carbon from the ocean's surface to its depths (Primeau et al., 2013 and Volk and Hoffert, 1985).

Archimedian pump

The process by which organic matter, such as dead phytoplankton and zooplankton, sinks from the surface to the deep ocean, carrying carbon with it, is referred to as the Archimedian pump, or "marine snow pump". The ancient Greek mathematician Archimedes, who established the buoyancy principle, is honoured in the name of this procedure. Because organic matter has a higher density than the surrounding water, it sinks, a phenomenon known as the Archimedian pump (Primeau et al., 2013 and Volk and Hoffert, 1985).

Reciprocating pump

The process of carbon transfer between the surface and deep ocean by means of the seasonal or periodic migration of organisms like fish, squid, and krill is referred to as the reciprocating pump. During periods of abundance, these organisms take in carbon by feeding on phytoplankton and other organic debris at the surface. This carbon is efficiently transported from the top to the deep ocean by them as they move downward to deeper waters (Primeau et al., 2013 and Volk and Hoffert, 1985).

It is unclear how much any of these processes contributes to open ocean habitats. Although the Archimedian pump is typically thought to predominate in total euphotic zone export, the diffusion pump may also play a significant role in some ecosystems. Physical (light, temperature, and turbulence) and biological (phytoplankton species composition, and growth) factors influence how quickly each component of the biological pump works (Takahashi et al., 2009).

2.1.2.3 : The soft tissue pump

It describes how the so-called remineralized DIC (organic particles that are remineralized back into DIC at depth) sinks. The physical transmission of the remineralized DIC back to the surface layer is also included in the three biological pumps. The combined effect of these pumps causes an excess of DIC in the deep ocean relative to the surface, and the DIC gradient between the surface and deep ocean serves as a natural gauge of their power. Additionally, this offers a more precise separation of the preformed DIC from the remineralized DIC, allowing for a more comprehensive analysis of the role of ocean circulation since the presence of preformed carbon at depth means that it has been subducted from the surface (Gruber et al., 2009).

Compared to winter, the spring and summer seasons are when the BCP is most effective in the SO. Both the SAZ and AZ are significant net CO₂ sinks throughout the growing season (spring/summer), with the biological pump outpacing the solubility pump (Gruber et al., 2009;

Takahashi et al., 2009; Mongwe et al., 2018). While the AZ turns into a CO2 source due to the confluence of a weak biological pump and the upwelling of CO₂-rich deep waters in the winter, the SAZ remains a CO₂ sink due to the dominant influence of the solubility pump (i.e., the cold surface temperatures) (Gruber et al., 2009; Takahashi et al., 2009; Mongwe et al., 2018).

Although the SAZ is a significantly stronger sink than the AZ, both the SAZ and the AZ appear to be CO₂ sinks over an annual cycle (of about 0.64 Pg C yr⁻¹ and 0.1 Pg C yr⁻¹, respectively) (Gruber et al., 2009; Takahashi et al. 2009; Landschützer et al., 2015; Mongwe et al., 2018). According to estimates by Cox et al., 2000 and Siegel et al., 2014, atmospheric CO₂ concentrations may be 50% higher than they are right now if it were not for the Southern Ocean's biological pump. The macronutrients (NO₃⁻ and PO₄³⁻) supplied from depth are never fully consumed in the mixed layer, causing the Southern Ocean to constitute a "leak" in the global ocean's biological pump despite its significant contribution to CO₂ drawdown (Weber and El-sayed, 1987; Priddle et al., 1998; Sigman and Boyle, 2000).

2.2: Carbonate system and buffering

Although the ocean's absorption of atmospheric CO₂ lessens global warming, it also alters the seawater's carbonate chemistry (de Carvalho-Borges et al., 2018). Since the start of the industrial revolution, the atmospheric CO₂ absorbed by the surface ocean waters has decreased pH by around 0.1 units, which is equivalent to an increase in acidity of about 30% (Sabine et al., 2004). Because of this, the concentrations of carbonate ions in surface waters have fallen by 15% in the SO and by 11% in the tropics (Orr et al., 2005). The pH and carbonate ion concentrations in surface waters will continue to decrease as atmospheric CO₂ levels rise. If the seas continue to absorb CO₂ from the atmosphere, further pH reductions of 0.3 to 0.5 units are predicted by the end of this century (Parry et al., 2007).

The carbonate system is one of the most crucial systems in the ocean since it is crucial for keeping the pH of the seawater within a specific range and regulating the atmospheric CO₂ (Egleston et al., 2010). At the air-sea interface, where oceanic CO₂ uptake from the atmosphere takes place (Figure 2.6), CO₂ is much more soluble than any other gas, including N₂, O₂, and Ar. When gaseous CO₂ dissolves in the ocean, the resulting aqueous CO₂ chemically reacts with water molecules (H₂O) in a matter of milliseconds to create carbonic acid (H₂CO₃), which can quickly split into bicarbonate ions (HCO₃⁻) and carbonate ions (CO₃²⁻) in a matter of sub-microseconds (Zeebe and Wolf-Gladrow, 2001). According to Heinza et al., (2015), seawater's biogeochemical behaviour as it travels through various oceanic systems regulates how much carbon is transferred in its dissolved form through currents, fronts, and turbulent mixing. As a result, carbon can be absorbed by the ocean and stored as

DIC, but DIC can also release gases into the atmosphere thanks to the chemical equilibrium mechanism that is detailed.



Figure 2.6: Schematic of marine carbon chemistry, demonstrating the uptake of atmospheric CO_2 and the reactions in seawater that form different "species "of the DIC pool. Modified from Samiento and Gruber, (2006)

Another essential parameter used to describe the carbonate system is the total alkalinity (TA), which is defined as the amount of acid needed to neutralize all bicarbonate and carbonate ions plus a few minor species (Equation 2.1).

TA=
$$[HCO_3^{-}] + 2[CO_3^{2-}] + [B(OH)_4^{-}] + [OH^{-}] - [H^{+}] + minor constituents (2.1)$$

The Total Alkalinity (TA) is dominated by carbonate alkalinity (the sum of the charges of carbonate and bicarbonate ions), but also includes contributions from borate and other minor species and can be simplified as shown in Equation 2.2.

$$CA = [HCO_{3}] + 2[CO_{3}]$$
(2.2)

The pH of the water is an integral part of the carbonate system and is defined as the negative logarithm of the hydrogen ion concentration. The presence of CO_3^{2-} ions acts as a buffer to the increase in CO_2 and H⁺, because the more CO_3^{2-} ions that are present to react with H⁺ ions, the less H⁺ ions are left in solution and the higher the pH. As pH and the concentration of CO_3^{2-} ions decrease, this buffering capacity decreases meaning that, for a given increase

in CO₂, more H⁺ ions remain in solution. There are several ways of quantifying the ocean's buffering capacity (Egleston et al., 2010), the most common being the Revelle factor which relates the fractional change in CO₂ to the fractional change in total DIC (Revelle and Suess,1957). The polar oceans are especially sensitive to ocean acidification as their low TA to DIC ratio reduces their carbonate buffering capacity (Egleston et al., 2010).

According to Sarmiento et al., (1998) and Orr et al., (2005), the SO is predicted to be a region largely influenced by global change with the polar marine ecosystems being relatively sensitive to carbonate changes. The absorption of CO_2 has changed the ocean chemistry since preindustrial times, reducing the pH and carbonate ion concentration (CO_3^{2-}), with high latitudes among the most affected areas (Caldeira and Wickett, 2003; Orr et al., 2005).

Since most biological activities, such as primary production, take place in oceanic surface waters, a change in the chemistry of surface waters could have huge impacts on the ecosystem structure (Egleston et al., 2010). The increase of atmospheric CO $_2(g)$ also increases the CO $_2$ (aq), which plays a major role in biological processes beneficial to those marine organisms that require inorganic carbon for fixation (Egleston et al., 2010).

Based on a large-scale observational review of the SO, which also considers the seasonal magnitude and variability of CO_3^{2-} and pH, predicted that SO aragonite under-saturation will occur in winter by the year 2030 (McNeil and Matear, 2007). Aragonite (CaCO₃) is a mineral carbonate, one of two normal, naturally occurring crystal types of calcium carbonate (calcite mineral being the other type) (Haldar and Tišljar, 2014). Egleston et al., (2010), found the lowest buffer values in the SO as this region is uniquely vulnerable to high levels of CO_2 .

2.3: Processes that control the carbonate chemistry in seawater

The processes that regulate DIC and TA in the ocean are numerous. When DIC and TA change, several mechanisms can alter the carbonate chemistry of an oceanic water parcel. These processes are shown in Figure 2.7. Environmental factors like organic carbon loading, dissolved oxygen content, temperature, and salinity affect each process' relative contribution to the overall system (Zeebe and Wolf-Gladrow, 2001). Total alkalinity (TA) is first affected by salinity, and further changes are brought on by biogeochemical processes including the creation or dissolution of calcium carbonate (Zeebe and Wolf-Gladrow, 2001). Since the main chemical species (HCO₃⁻, CO₃²⁻, and B(OH₄⁻)) that contribute to TA increase proportionally with increasing salinity, the influence of salinity on surface waters accounts for more than 80% of the overall fluctuation in TA (Lee et al., 2006). The charge balance in seawater and TA are strongly connected. One may say that DIC monitors changes in carbon whereas TA monitors charges.

In Figure 2.7, the various drivers of the change in DIC are schematically represented in terms of their strength and direction. Previous research such as Arrigo et al., (2008) and Williams et al., (2018), has demonstrated that biological processes including photosynthesis and respiration, as well as seasonal variations in the carbonate system in the SO and in the airsea CO₂ exchange, are largely explained by these biological processes.



Figure 2.7: Effect of various processes driving the variability of dissolved inorganic carbon (DIC) and total alkalinity (TA), such as the photosynthesis/respiration (DIC decrease/increase and a small TA increase/decrease); calcium carbonate formation/di dissolution (DIC reduces/increase by one and TA by two units); CO2 invasion from atmosphere increases DIC, and release of CO2 to the atmosphere decreases DIC and TA stays constant in both cases. The dashed lines represent pH as a function of DIC and TA (adopted from Zeebe and Wolf-Gladrow, 2001 without any modification)

DIC and fugacity of CO₂ (fCO₂) decrease during photosynthesis while pH and CaCO₃ saturation rise. Although TA is less impacted by photosynthesis than DIC (Figure 2.7), TA does increase significantly during photosynthesis due to nitrate and hydrogen ion consumption when proteins are produced (Equation 2.3). When calcium carbonate is produced, however, the TA change doubles that of the DIC (Equation 2.4). This means that only DIC changes if

there is no CaCO₃ production, but both TA and DIC change if CaCO₃ production happens concurrently with photosynthesis (Chapman et al., 2020).

$$2CO_2 + NO_3^- + H^+ + H_2O \rightarrow NHCH_2CO \text{ (org)} + 3.5O_2$$
 (2.3)

$$Ca^{2+} + 2HCO_3 \rightarrow CaCO_3(s) + H_2O + CO_2(aq)$$
(2.4)

As DIC is converted into organic matter during photosynthesis and respiration (Heterotrophic respiration), the concentration of DIC in the water decreases. Although they result in a minor rise or decrease in TA due to the digestion and remineralization of nutrients, photosynthesis and respiration do not directly affect carbonate alkalinity (Brewer and Goldman, 1976). When phytoplankton absorbs nitrate, they also absorb protons, raising the alkalinity of the solution. Therefore, the C:N ratio of the organic matter being created or respired determines the ratio of the effects of photosynthesis and respiration on DIC and TA. This ratio changes depending on the evolutionary history of the primary producer, growth rate, and nutrient availability (Redfield et al., 1963; Geider and La Roche, 2002; Quigg et al., 2003; Arrigo, 2005). It has been roughly calculated as 106:16 by Redfield et al., (1963).

Physical processes, such the mixing of subsurface water that is often high in CO $_2$ (low pH), are important for transporting CO $_2$ to the surface water, especially in the descent because of enhanced wind-induced mixing and water column cooling. With the interchange of the atmosphere and marine CO $_2$, the DIC, pCO $_2$, and pH levels also alter. When the ocean's pCO $_2$ is lower than the atmospheric level, atmospheric CO $_2$ is added to the water's CO $_2$ (referred to as an ocean sink in Figure 2.7), and if the ocean's pCO $_2$ is greater, it releases CO $_2$ into the atmosphere during ocean outgassing (referred to as an ocean source of CO $_2$ in Figure 2.7). Changes in uncharged CO $_2$ will not impact TA since TA depicts the ion-charge balance in the water (Figure 2.7). Seasonal warming and cooling have an impact on CO $_2$ solubility and contribute to the variability in pCO $_2$ and pH.

2.4: Ocean Acidification

Globally, the oceans play a key role in absorbing CO₂ from the atmosphere resulting in what is referred to as ocean acidification. Ocean acidification occurs when the ocean becomes acidic due to the pH of seawater being reduced by the uptake of atmospheric CO₂. On a global scale, the average pH of open ocean surface water is currently about 8.1 which means the ocean is slightly alkaline. It has declined from 8.2 to 8.1 between pre-industrial times and the

1990s and it is projected to decrease to 7.8 by the end of the century (Gattuso and Lavigne, 2009).

The reaction of the absorbed CO₂ with seawater (H₂O) produces carbonic acid. This chemical reaction also brings about many chemical changes in the chemistry of seawater (Figure 2.8). The complete reaction of CO₂ and H₂O brings about a reduction in seawater pH and the availability of carbonate ions. Carbonate ions are very important for shelled species, corals, marine plankton, and other calcifying species. When carbon dioxide dissolves in seawater a vast portion of it is transported into deeper waters through the thermohaline circulation and the biological pump. The remaining fraction of CO₂ forms carbonic acid and the net effect of the reaction is the increase in hydrogen ions and a drop in the pH of surface ocean waters (Figure 2.8) (Gattuso and Lavigne, 2009).

When the aragonite saturation state is below 1, the water is undersaturated concerning calcium carbonate (CaCO₃) minerals, and shells and skeletons of marine species such as corals, mussels, and oysters become defenceless to dissolution. The impacts of ocean acidification on marine life are understood in most of the species that require carbonates in their life stages. Marine-shelled species have been studied and predicted to be the most vulnerable organisms to ocean acidification (Figure 2.8). The reduction of carbonate ions makes it difficult for corals and other calcifying species to build hard substances e.g., shells and skeletons. The effects are also severe in other fish species.



OCEAN ACIDIFICATION

Figure 2.8: The process of ocean acidification as the ocean absorbs atmospheric CO2 (University of Maryland, 2018).

2.5: Southern Ocean Frontal zones and Water masses

The eastward-flowing ACC, which completely encircles Antarctica, dominates the SO's largescale circulation (Figure 2.9). The ACC divides the SO into different frontal zones; the Subtropical Zone (STZ), Subantarctic Zone (SAZ), Polar Frontal Zone (PFZ), and the Antarctic Zone (AAZ) via its associated hydrographic fronts (the Subtropical Front (STF), Subantarctic front (SAF), Polar Front (PF), Southern Antarctic Circumpolar Front (sACCF) and Southern Boundary (SBdy)) (Witworth and Nowlin, 1987; Orsi et al., 1995). The STF marks the northern edge of the SAZ, while the SBdy, which is not a dynamic front but is the southernmost extent of the Upper Circumpolar Deep Waters (UCDW), is located south of the sACCF (Figure 2.9).

The Subtropical Front (STF), which separates the Subtropical Zone (STZ) and the Subantarctic Zone (SAZ), is thought of as the Subantarctic Front (SAF's) northern border. In each SO basin, the currents connected to the Subtropical Front (STF) are extensions of the western border current (Deacon, 1982; Orsi et al., 1995). High salinity and temperatures in the Subtropical Front (STF) region both contribute to the development of mixed layer dynamics. Low levels of surface nutrients (i.e., nitrate) are present in this area, and the Subantarctic Surface Waters (SASW), which flow north and are covered by Subantarctic Mode Water (SAMW) and can be penetrated by the Subtropical Zone's (STZ's) thick mixed layer during the winter, provide nutrients to the STF (Talley et al., 2011). Subtropical Surface Waters (STSW), which are deficient in nutrients, also entrain into the STF from the north. The Subantarctic Front (SAF) creates the SAZ's southern edge, which is thought to be the ACC's greatest frontal zone (Orsi et al., 1995; Pollard et al., 2002).



Figure 2.9: Schematic showing the climatological positions of the Southern Ocean fronts; STF, SAF, PF, SACCF ASF (Antarctic Slope Front), and SB (Southern Boundary), and their respective frontal zones. Figure taken from Talley et al., (2011)

Subantarctic Mode Water (SAMW), which originates near the Subantarctic Front (SAF) as a result of wintertime cooling and mixing of Subantarctic Surface Water (SASW) and Subtropical Surface Water (STSW), is one of the upper Subantarctic Zone (SAZ) water masses. It can form as deep as 500 m below the surface. Toggweiler et al., (1991), Sarmiento et al., (2004), Marinov et al., (2006), Talley et al., (2011), describe the Subantarctic Mode Water (SAMW) as a thick layer with nearly uniform properties that subducts in the SAZ and flows northward to become a component of the permanent pycnocline, ultimately nutrient enriching the surface waters of the subtropical gyres. Antarctic Intermediate Water (AAIW), which is believed to have formed as a result of Antarctic Surface Water (AASW) sinking across the SAF, flows beneath SASW and Subantarctic Mode Water (SAMW). According to Talley et al., (2011), the Antarctic Intermediate Water (AAIW) is an abnormally low-salinity water mass that is still detectable as far south as 5°S in the Indian Ocean and 10-20°N in the Atlantic.

Antarctic Intermediate Water (AAIW) is covered by Antarctic Bottom Water (AABW), which is created in the Weddell and Ross Seas, as well as Upper and Lower Circumpolar Deep Water (UCDW and LCDW, respectively). Nutrients are supplied through vertical mixing with the

underlying thermocline and large-scale Ekman transport of Antarctic Surface Waters (AASW) originating in the Antarctic Zone (AZ) (Sarmiento et al., 2004). In the Subantarctic Zone (SAZ), temperature and not salinity plays a dominant role in the formation of the mixed layer (Pollard et al., 2002). In the centre of the Antarctic Circumpolar Current (ACC), the Polar Front (PF) serves as the border between the Polar Frontal Zone (PFZ) and the Antarctic Zone (AZ).

An abrupt shift from near-isothermal Subantarctic Surface Water (SASW) to the warmer, saltier waters of the Subantarctic Front (SAF) characterizes the Polar Frontal Zone (PFZ) between the Polar Front (PF) and the Subantarctic Front (SAF), which is a highly active zone (Talley et al., 2011). The Polar Frontal Zone (PFZ) is home to many powerful eddies that help with heat exchange between the north and the south. These eddies are created by the Polar Front (PF) and Subantarctic Front (SAF) meanders (Savchenko et al., 1978). The Antarctic Surface Water (AASW), Upper Circumpolar Deep Water (UCDW), Lower Circumpolar Deep Water (LCDW), and Antarctic Bottom Water (AABW) are some of the water masses in the Polar Frontal Zone (PFZ). Through the Ekman transport of Antarctic Surface Water (AASW), surface nutrients are advected northward from the Antarctic Zone (AZ) and into the Polar Frontal Zone (PFZ) (Sarmiento et al., 2004). The Ekman upwelling, which delivers nutrients to the surface, is another feature of the Polar Front (PF) (Meskhidze et al., 2007). Strong winds that propel the upwelling of Upper Circumpolar Deep Water (UCDW) are responsible for this nutrient upwelling (Whitworth and Nowlin, 1987).

The Open Antarctic Zone (OAZ) and Polar Antarctic Zone (PAZ), which are the northern and southern domains of the Antarctic Zone (AZ), respectively, are separated by the sACCF and are situated south of the Polar Front (PF) (Figure 2.10). The Open Antarctic Zone (OAZ) always has no ice, but the Polar Antarctic Zone (PAZ) has seasonal ice cover (Orsi et al., 1995). Although the southern Antarctic Circumpolar Current Front (sACCF) denotes the southern extent of Upper Circumpolar Deep Water (UCDW) (Talley et al., 2011), the Polar Antarctic Zone's (PAZ's) surface layer is underlain by Lower Circumpolar Deep Water (LCDW) (Whitworth and Nowlin, 1987; Sigman et al., 1999), and the Antarctic Zone (AZ) has similar water masses to the Polar Frontal Zone (PFZ) (Figure 2.10). As a result, while Lower Circumpolar Deep Water (UCDW) underlies the Open Antarctic Zone (OAZ) surface, it is largely absent from the Polar Antarctic Zone (PAZ). Because some North Atlantic Deep Water (NADW) is included in Lower Circumpolar Deep Water (LCDW), it has a lower NO3⁻ concentration than Upper Circumpolar Deep Water (UCDW) and a higher salinity and oxygen content. A typical midsummer Antarctic Zone (AZ) phenomenon is the establishment of a temperature minimum (T_{min}) layer, when the winter's low-temperature surface layer turns into the subsurface water mass beneath the summer mixed layer. The Tmin, which reflects the starting state from which the surface Antarctic Zone (AZ) evolves throughout the summer

(Altabet and Francois, 2001), is frequently referred to as a summertime record of winter conditions. Upper Circumpolar Deep Water (UCDW) upwelling, which is fuelled by Ekman divergence, transports nutrients to the Antarctic Zone (AZ) surface from depth in conjunction with winter cooling and sea-ice development (the latter in the PAZ), which cause the mixed layer to thicken. Due to iceberg movement and sea ice melting in the spring and summer, greater nutrient concentrations (such as iron) are observed in the AZ, exacerbating seasonal mixing-driven nutrient dynamics (Lannuzel et al., 2016).

The PAZ is part of the marginal ice zone (MIZ), which is a biologically active area of unconsolidated sea-ice cover (Orsi et al., 1995). The MIZ, which spans hundreds of thousands of square kilometres (km²) and is a hydrodynamically and biogeochemically complex region of the Southern Ocean, exhibits significant seasonal waning and waxing. The MIZ extent is at its lowest point in the summer (about 1.8 million km²) (Turner et al., 2017; Meehl et al., 2019), whereas the sea-ice extent is at its highest point in late winter (around 12 million km²) (Turner et al., 2017). According to Lannuzel et al., (2016), phytoplankton blooms are said to occur in conjunction with sea ice melting in the spring and summer due to freshening that stratifies the upper layer and an increased availability of iron.



Figure 2.10: The circulation and direction of the water mass flow in the SO. Subtropical Front (STF), Subantarctic Front (SAF), Polar Front (APF), southern ACC Front (sACCF), Southern Boundary (SBdy), Subtropical (ST), Subantarctic (SANT) and Antarctic Domain (ANT) Modified from (Koubbi et al., 2017)

2.6: Classification of Fronts along the Good Hope transect

The primary frontal bands of the Southern Ocean (SO) have a substantial zonal component, and the placement and flow patterns of the various frontal systems that divide the various ACC zones heavily influence the SO's spatial organization. Over the past three decades, numerous measurements have been taken in the Southern Ocean's South Atlantic and South Indian sectors (Ansorge et al., 2004). The frontal characteristics along the Greenwich Meridian line are less intense and variable, as can be inferred from the altimetry and historical hydrographic data, in contrast to other regions of the SO, where the frontal system displays high bands of variability with enhanced eddy activity, such as at the Drake Passage and South Georgia, at the South-West Indian Ridge (Ansorge and Lutjeharms, 2003), and south of Australia (Sokolov and Rintoul, 2002). The Subtropical front (STF) has the most pronounced annual cycle, while the Subantarctic front (SAF) and particularly the APF show smaller seasonal shifts, according to research by Billany et al., (2010) into the seasonal variability of the locations of the ACC front at the Greenwich Meridian (Figure 2.11). From May through August, the STF position rapidly shifts as this front advances north.



Figure 2.11: Mean seasonal meridional shifts (Latitude) in the frontal positions in the ACC at the Greenwich Meridian from 20 years continuous time-series. The Error bars represent the standard deviation for each month within the seasonal mean a) Subtropical front, b) Subantarctic front, c) Antarctic polar front, d) Southern ACC front, e) Southern Boundary front (Billany et al., 2010)

To track the upper-level circulation linked to the baroclinic shear, the main ACC fronts must be identified. Table 2.1 provides definitions for the axial values (depth axis) at 200 m depth as well as the surface and subsurface (200 m depth) ranges.

Front	Surface range	Subsurface range
STF	10.6 - 17.9⁰C; 34.3 - 35.5 psu	8.0 - 11.3⁰C; 34.42; Axial value: 10⁰C, 34.8 Psu
SAF	6.8 - 10.3⁰C; 33.88 - 34.36 psu	4.8 - 8.4ºC; 34.11 - 34.47 psu; Axial value: 6.0ºC, 34.3 psu
APF	2.5 - 4.1ºC	Axial value: 2ºC

Table 2.1: Definitions of the fronts bordering the ACC. (adapted from Belkin and Gordon, 1996)

2.6.1 : The Subtropical Front (STF)

Warm, salty Subtropical Surface Waters (STSW) and cooler, fresher Subantarctic Surface Waters (SASW) are separated by the Subtropical Front (STF). It is both the most northerly and noticeable surface thermal front linked with the Antarctic Circumpolar Current (ACC) (Graham and De Boer, 2013). The average position of the STFs in the South Atlantic section of the SO is found to be between 41 and 40°S, according to data compiled from over 80 crossings of the STF (Lutjeharms and Valentine, 1984). According to recent research done in winter 2015 along the Good Hope transect, the STF's surface expression was detected between 39.39 and 40.54°S, while its subsurface core was located around 40.42°S (Du Plessis et al., 2017).

2.6.2 : The Subantarctic Front (SAF)

In contrast to the Subtropical Front (STF), the Subantarctic Front (SAF) and Antarctic Polar Front (APF) of the ACC are associated with vertical shear that typically extends throughout the water column. The Polar Frontal Zone (PFZ), a region between Subantarctic Surface Water (SASW) and Antarctic Surface Water (AASW), has the Subantarctic Front (SAF) as its northern limit. The SAF is less distinct in its surface expression when compared to STF, which is distinguished by a strong and constant gradient in both surface and subsurface expressions, making identification simple (Ansorge et al., 2005). Due to the weak nature of this front, it may be challenging to pinpoint the exact PFZ limits. The salinity minimum of the AAIW is more pronounced north of the SAF than south of the SAF, where it is weak or nonexistent. The most vertically oriented isotherm inside a temperature gradient between 3°C and 5°C, with its

surface expression spanning between 8°C and 4°C, can be used to identify the SAF, which is primarily a subsurface front. The subsurface axis of this front has been estimated by recent studies to be near 43.49°S during winter (Du Plessis et al., 2017). According to Swart et al., (2010), the SAF is frequently observed in the south Atlantic as a wide frontal band that spans 250 km (43.38°S - 47.17°S) and has several narrow reversals.

2.6.3 : Antarctic Polar Front (APF)

The APF delineates the northern boundary of the Antarctic Zone (AZ), and the northern limit of the 2°C temperature minimum at a depth of 200 m historically served as a marker for the APF's subsurface expression (Ansorge et al., 2005). In some cases, this does not match the APF surface expression, and the surface expression is instead shown by the highest temperature gradient between 6°C and 2°C. The APF is distinguished by a shallow temperature minimum connected to the Winter Water (WW) remains, which is located between 50 and 150 m. It varies according to the season in such a way that in the winter it is practically homogeneous and extends to a depth of 250 m, whereas in the summer the mixed layer only reaches a depth of 50 to 100 m, resulting in a distinct subsurface T_{min} . This water mass has an APF temperature range of -1.8 to 6°C and a salinity range of 33.4 to 34.2 psu (Ansorge et al., 2005). The subsurface expression of the Antarctic Polar Front (APF) was found to lie at 50.36°S, according to a previous crossing of this front in winter 2015 (Du Plessis et al., 2017).

2.6.4 : Southern Antarctic Circumpolar Current Front (sACCF)

The extensive circumpolar front (sACCF) is located south of the APF. This front is located at roughly 65°S, where the atmospheric low-pressure belt Antarctic trough that divides the westerly and easterly wind belts is located (Ansorge et al., 2005). In contrast to the other fronts connected to the ACCC, the sACCF is determined by the UCDW's temperature and salinity characteristics rather than dividing discrete surface water bodies. Two branches of this front have been found by prior research (Orsi et al., 1995) in the South East Atlantic region of the SO as being characterized by a strong salinity gradient (33.80 - 33.63 psu) at 63.40°S and between 33.78 - 33.09 psu at 64.7°S with a temperature between 0.9 - 0.7°C. The 0°C isotherm along the T_{min}, which places the front at a mean position of 63.48°S, has been used to identify the sACCF south of Australia. However, the south Atlantic sector of the SO experiences warming of the surface mixed layer and northern extent of the Tracer Mixing Line cooler than 0°C as a result of the increase in air temperature between December and February, creating a credible indicator of the location of the sACCF. By this definition, the winter 2015 sACCF was located at 55.44°S (Du Plessis et al., 2017).

Over the years, various techniques for locating fronts and their placements have been used (using sea surface height or temperature, salinity and Chlorofluorocarbons to classify fronts). Both physical and biological processes in the SO are directly impacted by the placement of fronts. Temperature and salinity are necessary for the identification of fronts as water mass boundaries. Five classical fronts have been established in the SO using fronts as physical boundaries between water masses (Orsi et al., 1995). The southern ACC Front, Subtropical Front, Antarctic Polar Front, and Southern Boundary Front. It is claimed that each of these fronts is circumpolar and continuous (Orsi et al., 1995).

According to Pollard et al., (2002), variations in water masses across SO fronts are correlated with changes in the stratification of the water column. Due to significant surface heating, surface waters are warm in northern regions, but the deep ocean is isolated from this heating and is consequently chilly. Here, temperature is the primary factor in the stratification of the water column. The difference in temperature between the ocean's surface and its depth is smaller closer to the pole because surface heating is less intense. In the Polar Regions, salinity predominates in the stratification of the water column. According to Pollard et al., (2002), deep waters are more acidic than surface waters.

The region's ecology and biogeochemical cycles, which affect the climate system, are greatly affected by the SO's unusual oceanographic conditions. Deep-water masses (so named because they exist at depths greater than 1 km throughout much of the global ocean) rich in nutrients and CO₂ upwell to the ocean surface in the SO as a result of its steeply sloped isopycnals. Once they reach the ocean's surface, these once deep waters can exchange heat and CO₂ with the atmosphere and euphotic zone organisms to make use of their nutrients (Yamazaki et al., 2021). The 'mixing barrier' effect for frontal jets prevents the exchange of tracers across fronts, and the fronts act as regions of increased vertical exchange between the deep and surface ocean, they are two fundamental mechanisms by which SO fronts are thought to play a key role in the global distribution of essential nutrients like nitrates. In most of the global ocean, less dense, nutrient-poor water masses are vertically piled on top of denser, nutrient-rich water masses. Vertical property gradients in the SO, however, move laterally and become horizontal property gradients as a result of considerable upwelling (concentrated in frontal zones). These upwelled waters cannot combine with adjoining nutrient-poor water masses to produce biogeochemical fronts because of the mixing barrier effect (Yamazaki et al., 2021).

As a result, it is yet unclear how filamented, dynamic fronts would affect nutrients and other tracers. Recent studies have shown that upwelling and subduction in the SO are controlled by the intricate interplay between frontal jets, enormous bathymetric features, and surface winds.
Thus, only regions where fronts and bathymetry combine can experience nutrient upwelling and CO₂ subduction into the interior of the ocean.

2.7: Distributions of nutrients in the Southern Ocean

The SO is referred to as a High-Nutrient, Low-Chlorophyll (HNLC) region since it is widely known for the partial removal of euphotic zone macronutrients nitrate (NO₃⁻), silicate (SiO₄), phosphate (PO₄³⁻), and nitrite (NO₂⁻) during the growth season. Primary Productivity (PP) in the SO is frequently discussed in the context of the "Antarctic Paradox" (Priddle et al., 1992; Tréguer and Jacques, 1993), which refers to the fact that mixed-layer macronutrients are never fully utilization by phytoplankton, creating productivity (i.e., biomass accumulation and export) lower than the available macronutrients suggest it should be.

It is generally accepted that a combination of iron and light limitation is responsible for phytoplankton's failure to completely assimilate surface macronutrients (Martin, 1990; Nelson and Smith, 1991; Sunda and Huntsman, 1997). According to Henley et al., (2020), SO macronutrient cycling has a robust seasonal cycle that is controlled by both physical and biological factors. Deep mixed layers that pull nutrients from depth into surface waters are a hallmark of winter. The deep mixed layers and low solar radiation during this season result in a shortage of available light, delaying the consumption of the nutrients. According to research (Pollard et al., 2002; Sarmiento et al., 2004), the macronutrient silicate (SiO₄) limits some phytoplankton between the STF (perennially) and the northern PF (seasonally), where its concentration averages 5 μ M (Henley et al., 2020).

Mixed-layer ambient SiO₄ concentrations of 24-78 µM are frequently seen south of the Polar Front (PF) (Henley et al., 2020), so SiO₄ limitation does not exist there. These elevated SiO₄ concentrations come from Circumpolar Deep Water (CDW) that upwells close to the ACC. Diatoms, an ecologically significant group of phytoplankton, are severely impacted by SiO₄ deficiency because they need dissolved SiO₄ to biomineralize their opal (i.e., amorphous biogenic silica) frustules. Diatoms are a key direct driver of the biological pump in the Southern Ocean and throughout the world because of their comparatively dense opal shells, which efficiently permit carbon export from surface waters when they sink (Buesseler, 1998).

An exception to this is that smaller diatom species are more effective carbon exporters, whereas big, strongly silicified diatoms in the iron-limited Southern Ocean have been reported to decouple carbon and SiO₄ drawdown, eliminating SiO₄ more effectively than carbon (Assmy et al., 2013). Given that diatoms are also regarded as NO₃⁻ specialists (Litchman et al., 2006; Fawcett and Ward, 2011), this phytoplankton group considerably contributes to export production in accordance with the new production paradigm (Tréguer and Pondaven, 2000).

Because diatoms preferentially use SiO₄ over NO₃⁻ in AASW (i.e., in a ratio >1:1, which is the ratio expected for optimally growing diatoms) there is a SiO₄ limitation in the Subantarctic region of the Southern Ocean (i.e., the combined SAZ and PFZ between the STF and PF). This preferential SiO₄ absorption occurs mostly in the AZ under iron-limited circumstances. Because of this, the northward-flowing AASW is rich in NO₃⁻ and PO₄³⁻ but deficient in SiO₄ (Sarmiento et al., 2004; Henley et al., 2020), which encourages the growth of non-diatom phytoplankton such dinoflagellates, prymnesiophytes, and cryptophytes. Since non-siliceous phytoplankton species tend to sink more slowly than opal-ballasted diatom species north of the AZ, their dominance has consequences for the biological pump (Buesseler, 1998).

As a result, the Southern Ocean's SiO₄ limitation of diatoms may be a wasted chance for carbon drawdown (Brzezinski et al., 2003). AAIW and SAMW that flow northward are SiO₄- depleted as a result of the preferential removal of SiO₄ compared to NO₃⁻ and PO₄³⁻ south of the PF (Sarmiento et al., 2004). The ratio in which these waters (SAMW in particular) subduct at their formation locations determines the amount of nutrients that they feed to the thermocline of the low-latitude ocean (Toggweiler et al., 1991).

Thus, the composition of phytoplankton communities in the low latitudes and the North Atlantic, as well as the potential for N₂ fixation, are significantly influenced by iron-limited diatoms in the polar Southern Ocean (Weber and Deutsch, 2010). That is, because SAMW is SiO₄-depleted, it cannot support the growth of high diatom abundances when it upwells in the subtropical ocean. According to Weber and Deutsch, (2010), low-latitude phytoplankton may be more strongly N-limited than previously thought, which would increase the need (i.e., the environmental selection pressure) for N₂ fixation. The subsequent consumption of NO₃⁻ and PO₄³⁻ by non-diatom phytoplankton tends towards a ratio of 20:1.

3.1: Study area

The Southern oCean seAsonaL Experiment (SCALE) spring cruise was conducted from Cape Town to the spring ice edge (SIE) in the south Atlantic sector of the SO onboard RV S.A. Agulhas II from the 12th of October to the 19th of November 2019. The sampling stations were spatially sampled at approximately 2 degrees apart and were conducted in two transects as follows; The Southeast transect, was conducted along the spring marginal ice zone (MIZ) from 55.001°S, 0.0°E to 58.4°S; 22.0°E (station labelled MIZ; Figure 3.1) and South to North transect, was conducted along the GEOTRACES GIPY04 transect (stations labelled GT, including PUZ and SAZ2 stations; Figure 3.1) from the spring marginal ice (55.91°S; 0.18°E) to the subtropical zone (38.61°S; 11.83°E).

Along the Southeast transect, there was MIZ South and MIZ East transects, where MIZ South stations were sampled along the Greenwich meridian from latitude 55.001 to 59.31°S (which includes MIZ0A, MIZ2 and MIZ3 stations) within the Weddell Gyre of the Antarctic zone (AAZ). The MIZ East stations were sampled within the eastern part of the Weddell gyre and included MIZ4, MIZ5, MIZ6, MIZ7 and MIZ9 stations. Due to ice cover along this transect, the stations were sampled from near the surface to 500 m depth.

Along the South to North transect, the stations were sampled from near the surface to near the sea floor. The cruise track crossed important SO Antarctic Circumpolar Currents (ACC) from the spring ice edge to the subtropical. The frontal positions were identified at the position where the cruise crossed that front using the mean absolute dynamic topography and satellite altimetry data set, following the method by Swart et al., (2010). From South to North, these includes the Southern Boundary (SBdy; 56.21°S; 0.09°E), southern Antarctic Circumpolar Current Front (sACCF; 52.37°S; 0.00°E), Antarctic Polar Front (APF: 49.29°S; 2.40°E), Subantarctic Front (SAF: 44.69°S; 6.92°E) and the Subtropical Fronts (STF; 40.59°S; 10.35°E). The zone south of the PF was defined as the Antarctic Zone (AAZ) where GT1, GT2B, GT3, and PUZ stations were conducted. Between APF and SAF lies the Polar Frontal Zone (PFZ), where stations GT4, GT5 stations were conducted. Between SAF and STF, there lies the subantarctic zone (SAZ) where GT6, GT7B and SAZ2 stations were conducted. North of the STF lies the subtropical Zone (STZ), where GT9 and GT8 stations were conducted. To further characterize the South to North transect, we used STF and PF positions as cut-offs between the three Southern Ocean domains; The Subtropical (ST; includes GT8 and GT9

stations), Sub-Antarctic (SANT; includes GT4, GT5, GT6 and GT7B stations), and Antarctic (ANT; includes GT1, GT2B, GT3 and PUZ stations) domains (Figure 3.1).



Figure 3.1: Cruise track and stations where sampling took place along the Southeast and South to North transects. The dots represent the stations. The STF represents the Subtropical Fronts, SAF represents the Subantarctic Front, APF represents the Antarctic Polar Front, the sACCF represents the southern Antarctic Circumpolar Current Front, and SBdy represents the Southern Boundary and the MIZ represent Marginal Ice Zone. The three oceanographic domains considered are the Subtropical (ST), Sub-Antarctic (SANT), and Antarctic (ANT) (produced using ODV: Schlitzer and Mieruch, 2021)

3.2: Sample collection and processing

During this cruise, CTD profiles for seawater sampling were conducted in two ways; i) from near the surface (20 m) to 500 m or 1000 m depth during the Southeast transect, and ii) from near the surface to near the seafloor (maximum of 4500 m) during South to North transect.

3.2.1 : Dissolved Inorganic Carbon (DIC) and Total Alkalinity (TA)

At each sampling location, seawater samples for DIC and TA analysis were taken from 24 \times 12 L Niskin CTD rosette (General Oceanics; Seabird, SBE 911plus). To avoid additional biological change in the sample, samples were spiked with 100 μ L of concentrated HgCl₂ (Mercuric Chloride, Merck SA). The DIC samples were analyzed onboard using Marianda's VINDTA 3C (Versatile Instrument for the Determination of Titration Alkalinity). The VINDTA

measures CO₂ colometrically and estimates total alkalinity by potentiometric titration from the same sample. Using the CRMs (Certified reference Materials supplied by Dr. Andrew Dickson of United States Scripps Institution of Oceanography), all DIC samples were adjusted. Table 3.1 provides information on the CRMs' measurements of salinity, DIC, and TA.

Station	Salinity (psu)	ΤΑ (μΜ)	DIC(µM)
SAZ2	34.10	2277.13	2128.89
PUZ	34.22	2313.75	2204.38
MIZO	34.23	2315.32	2203.26
MIZ1B	34.38	2332.76	2241.54
MIZ2	34.46	2322.84	2238.59
MIZ3	34.49	2338.07	2244.74
MIZ4	34.48	2333.50	2245.23
MIZ5	34.48	2340.34	2256.49
MIZ6	34.51	2340.81	2242.65
MIZ7	34.39	2332.47	2228.83
MIZ9	34.26	2321.87	2228.20
GT1	34.36	2325.52	2233.19
GT2B	34.33	2322.04	2216.55
GT3	34.29	2313.36	2215.66
GT4	34.27	2306.15	2193.04
GT5	34.23	2296.57	2182.01
GT6	34.29	2296.98	2175.94
GT7B	34.61	2306.27	2168.31
GT8	34.72	2294.88	2113.40
GT9	34.79	2313.83	2149.40

Table 3.1: CRMs Salinity, TA, and DIC measurements at each station

3.2.2 : DIC and TA normalization

The DIC and TA concentrations normalized by salinity were used to study biological processes independent of variations related to evaporation or precipitation. At global scales, it is common

to apply S = 35 psu (Millero, 2007). In this study, we normalized both DIC and TA to the mean salinity of 34.397 psu.

3.2.3 : Nutrients

At the same depth where DIC and TA were sampled, seawater samples were taken for measurements of the macronutrients (NO_{3⁻} + NO_{2⁻}, SiO_{4⁴⁻} and PO_{4³⁻}). For additional investigation on land at the University of Cape Town, about 40 ml of seawater samples were collected into sterile 50 ml falcon plastic tubes (Merck, SA) and stored frozen at -20°C (Raguel Flynn; UCT-SA). Within two to three months of the voyage, the concentrations of $NO_3^{-} + NO_2^{--}$ and SiO4-4- were measured using a Lachat QuickChem flow injection analysis platform on land at the University of Cape Town in accordance with published auto-analysis methods (Diamond, 1994; Grasshoff, 1976) in a setup with a detection limit of <0.1 µM. On several days, duplicate samples were measured. After every ten samples, standards of varied concentrations were run to check instrument performance and allow for any drift to be corrected. The contents of PO43- and NO2- were measured in duplicate using a Thermo Scientific Genesis 30 Visible spectrophotometer onboard the ship with detection limits of <0.1 µM and 0.05 µM for PO₄³⁻ and NO₂⁻, respectively (Strickland and Parsons, 1968; Bendschneider and Robinson, 1952; Parsons et al., 1984). To guarantee the precision of the measurements, certified reference materials (JAMSTEC) were included at the start and finish of each run (Lachat and manual).

3.2.4 : Chlorophyll-a

For the Chlorophyll-*a* (Chl-*a*) study, seawater samples were taken from the upper surface waters at 6 different depths, 20 L of saltwater were filtered through filters with a 0.7 µM particle size (GFF, Whatman, Merck SA). After that, filters were put into glass vials with 90% acetone and kept in the dark at -20°C for 24 hours. Before sample analysis, samples were given time to acclimate to room temperature. The analysis was carried out using a Turner 10-AU Fluorometer (Turner Designs), which was calibrated prior to the trip using a standard calibration curve of raw Chlorophyll-*a* (Sigma C6144).

3.3. Ancillary dataset

Temperature (θ ; °C), Salinity (psu), Oxygen (μ M), Density (σ_{θ} ; kg/m³), and Fluorescence (mg/m³) measurements were obtained from the CTD sensors (Seabird, SBE 911plus). Oxygen from the CTD sensor was calibrated against the discrete bottle data measured using the Winkler Titration method. CTD fluorescence was corrected using discrete Chl-*a* measurements measured using a fluorometer (Turner 10-AU fluorometer; Turner design). Salinity was corrected using discrete samples analysed on Portasal Salinometer (8410A,

Portal Salinometer; UCT). CTD oxygen sensor was calibrated using in-situ dissolved oxygen measurement analysed by following Winkler Titration method. Potential density from the CTD dataset was used to calculate MLD for each station following the literature method reported by de Boyer Montegut et al., (2004), where the density differs from the density at 10 m by more than 0.03 kg/m³. Water column distribution of temperature, salinity and density measurements were used to characterize different water masses observed along the transects.

3.3.1. Apparent Oxygen Utilization (AOU)

The quantity of oxygen delivered to or taken from the water parcel by biological activity since it last achieved atmospheric equilibrium is measured using apparent oxygen utilization (AOU). Equation 3.1 was used to determine AOU in accordance with Weiss, (1970) description using temperature and salinity observations (Ito and Follows, 2005),

$$AOU = O_2$$
, sat (T, S) - [O₂] (3.1)

where AOU is expressed in μ M, T is the in-situ temperature (°C), S is the in-situ salinity (psu), O₂, sat is the surface saturated O₂ concentration as calculated for the corresponding in-situ temperature and salinity, and [O₂] is the in-situ measured O₂ concentration, expressed in μ M (Redfield, 1934; 1942). If AOU is positive, oxygen has been removed from the water parcel by biological activity.

3.4: Statistics

All statistical approaches to measure the significant differences were calculated using a t-test of two samples assuming unequal variance and one-way analysis of variance (ANOVA) single factor, with significant results reported at the 95% confidence level (alpha = 0.05).

4.1: Hydrographic context

The South to North transect (along the GIPY04) is the most important transect in this study, thus it will be presented first in all the sections. Temperature (θ ; $^{\circ}$ C), salinity (S; psu), and density (σ_{θ} ; kg/m³) were used to characterize the water masses observed along the transect.

4.1.1 : Water masses

4.1.1.1 : South to North transect

The water masses sampled along this transect are shown in Figure 4.1. In the subtropical domain, the warmest and saltier waters of Subtropical Surface Water (STSW: $12 > \theta < 24^{\circ}$ C; and 35.1 > S < 35.5 psu) above 500 m depth and Subantarctic Mode Water (SAMW; $26.4 > \sigma_{\theta} <$ 26.6 kg/m³; 14°C and 35.4 psu) below were observed (Figure 4.1). Their southern extent is limited by the Subtropical Front (STF) and the Subantarctic Front (SAF), respectively. The Subantarctic Mode Waters (a thick layer of homogeneous waters caused by wintertime surface convection) was found beneath the saltier and warmer Subtropical Surface Water down to 700 m depth. The Antarctic Surface Waters (AASW; 33.7 > S < 34.6 psu and $-1.9 > \theta < 4^{\circ}C$) was observed in the upper 200 m depth south of the Antarctic Polar Front and are composed of a remnant subsurface tongue of cold water produced in winter (Winter Waters; WW) and warmer surface water produced in spring. The northward subduction of the Antarctic Surface Waters within the Polar Frontal Zone creates an intermediate water called the Antarctic Intermediate Waters (AAIW; $27.0 > \sigma_{\theta} < 27.4 \text{ kg/m}^3$; $2 > \theta < 10^{\circ}$ C and 33.8 > S < 34.8 psu) (Figure 4.1 a,b, and c). This water mass is characterized by a salinity minimum that deepens northward to about 1400 m depth. Below the AAIW, at a depth greater than 1500 m, is the circumpolar deep waters (the largest Antarctic water mass by volume), originating from the North Atlantic Deep Waters (NADW; S > 34.8 psu) (Figure 4.1c). This water mass is further split into less dense Upper Circumpolar Deep Waters (UCDW; $\sigma_{\theta} = 27.6 \text{ kg/m}^3$) and the denser Lower Circumpolar Deep Waters (LCDW; $\sigma_0 = 27.8 \text{ kg/m}^3$) that shoal beneath the AASW layer south of 55°S. The Upper Circumpolar Deep Water is characterized by an oxygen minimum and nutrient maximum, while the Lower Circumpolar Deep Water has a salinity maximum, and both have high levels of DIC. The very cold, high saline, and more dense Antarctic Bottom Waters (AABW; 27.85 > σ_{θ} < 27.86 kg/m³; $-1 > \theta < 0^{\circ}$ C and 34.64 > S < 34.72 psu) are in the deep waters of the Southern Ocean. Its Antarctic origins mean that it has high oxygen, low temperature, and low salinity, relative to the overlying Circumpolar Deep Water. The mixed layer depths (MLD) shoal northwards, ranging from 167.42 m (at PUZ) to 17.86 m (at GT7B).



Figure 4.1: Water column distribution of a) Density (kg/m³), b) Temperature (°C), and c) Salinity (psu) with latitude along the South to North transect

4.1.1.2 : The Southeast transect.

Figure 4.2. shows the different water masses sampled along MIZ south and MIZ East transects, respectively. Along the MIZ south, a less dense (27.3 > σ_{θ} < 27.4 kg/m³, especially at MIZOA), more colder (θ > -1.5°C) and more saline (< 34.0 psu) Antarctic Surface Water was

observed from surface to 150m depth (Figure 4.2a, b and c). One of the interesting features was the observed dilution of saltier Antarctic Surface Water at MIZ2 to MIZ1B stations, with salinity minimum within rather light and fresh surface waters (15 > S < 30 psu) (Figure 4.2c), as a result of melting spring ice. Below this water mass, a southward shallowing end of the UCDW tongue ($\sigma_{\theta} = 27.6 \text{ kg/m}^3$) was observed at a depth between 60 to 140 m, and the LCDW ($\sigma_{\theta} = 27.8 \text{ kg/m}^3$) at a depth between 150 m to greater depths (Figure 4.2a, b and c). At greater depths (below 200 m depth), a denser ($\sigma_{\theta} > 27.8 \text{ kg/m}^3$), warmer ($\theta > 0.5^{\circ}$ C contour) and les saltier to fresh waters (0 > S < 30 psu contour) representative of the Antarctic Bottom Waters (AABW) was identified (Figure 4.2a, b and c).

During MIZ East, MIZ8 station was not sampled due to instrumentation maintenance thus the blank space between MIZ7 and MIZ9. Along MIZ East transect (MIZ4 to MIZ9), a very cold (θ < -1.0°C contour) and more saline (34.4 > S < 34.5 psu contour) winter waters (WW) with slightly low density (σ_{θ} < 27.6 kg/m³ contour) were observed at the surface down to about 100 m depth. Below this depth, lies tatches of fresher, less saline (< 34.0 psu contour), slightly warmer (θ > -1.5°C contour) and less dense (27.3 > σ_{θ} < 27.4 kg/m³ contour) waters at MIZ4, MIZ6, MIZ7 and MIZ9 from surface to about 150m depth (Figure 4.2d, e and f). The patches of fresher and less saltier waters are due to the melting spring ice. Below these water masses, a southward shallowing end of the warm (-1 to -0.25°C contour), saltier (> 30 psu contour) and highly dense UCDW (σ_{θ} > 27.6 kg/m³ contour) at a depth between 110 to 170 m and the LCDW (σ_{θ} > 27.8 kg/m³) were observed at a depth between 150 m to 500 m depths (Figure 4.2). Another interesting feature was the observed vertical upwelling of fresher and less saline (S < 30 psu contour) waters at MIZ6 station, probably resulting from melting of deep spring ice due to the observed warmer waters (Figure 4.2d, e and f).



Figure 4.2: Plot of water column distributions a and d) Density (kg/m³), b and e) Temperature (°C), and c and f) Salinity (psu) along MIZ East and MIZ South showing different water masses sampled

4.1.2 : Water column distribution of Dissolved Oxygen (DO) and Apparent Oxygen Utilization (AOU)

4.1.2.1 : South to North transect

Figure 4.3 shows the water column distributions of DO and AOU concentrations along the South to North transect. The DO concentrations were high at the surface and decreased to lower values at intermediate waters, followed by a slight increase in concentrations at greater depth, while AOU showed an opposite distribution to DO. At the upper surface waters, the DO concentrations and AOU ranged between 139 to 536 μ M and -190 to 188 μ M, respectively. Within the water column, the low DO values created a region called the minimum oxygen zone (MOZ), which was observed within the UCDW ($\sigma_{\theta} = 27.9 \text{ kg/m}^3$), with DO concentrations less than 180 μ M (Figure 4.3a), while the AOU concentrations were high within this water mass reaching the value of 180 μ M (Figure 4.3b). Further south at PUZ station, the DO values were

less than 210 μ M within the minimum oxygen zone, while AOU values reached about 200 μ M (Figure 4.3a and b). This minimum oxygen zone was due to the spring melting ice. One of the interesting features was the high upper surface DO concentrations (ranging between 375 to 475 μ M depth between 200 m to near the surface) observed between stations GT2 to GT4. The opposite was observed for AOU (concentration ranging between -190 to -50 μ M), where surface production has raised oxygen concentration above saturation.



Figure 4.3: Water column distributions of a) DO (μ M), and b) AOU (μ M) along South to North transect

4.1.2.2 : Southeast transect

Figure 4.4 shows the water column distributions of dissolved Oxygen and Apparent Oxygen Utilization along MIZ south (Figure 4.4a and b) and MIZ east (Figure 4.4c and d), respectively. Along both transect, there is high dissolved concentrations in the upper surface waters (AASW

and UCDW) than in the bottom waters (LCDW and AABW). The upper surface distributions of DO concentrations along this transect was statistically significantly higher than during South to North transect (t-test; p < 0.05), with concentrations reaching to about 400 μ M while AOU was low (< 100 μ M) (Figure 4.4 a, b, c and d). At intermediate and deeper depths, the DO concentrations decreased to lower values (ranging between 150 to 225 μ M), while AOU increased to values ranging between 125 to 225 μ M (Figures 4.4a, b, c and d).



Figure 4.4: Water column distributions of a) DO (μ M), and b) AOU (μ M) for MIZ South and c) DO (μ M), and d) AOU (μ M) for MIZ East transects

4.1.3 : Water column distribution of Macronutrients and Chlorophyll-a concentrations

4.1.3.1 : South to North transect

Figure 4.5 shows the water column distributions of macronutrients (DIN, silicate (SiO $_{4}$ -4) and phosphate (PO $_{4}$ ³⁻)) and Chlorophyll-a concentrations. In general, the water column distributions of macronutrient concentrations were typical of the Southern Ocean behaviour observed in austral summer and winter (Le Moigne et al., 2013; Mtshali et al., 2019), with low concentrations at the upper surface water that increased with depth. Sea surface distributions of macronutrients concentrations display a northward decrease from PUZ to GT9 station, with DIN concentrations ranging between 0.41 to 29.68 μ M, SiO $_{4}$ -4⁻⁴ ranging between 1.21 to 70.07 μ M and PO $_{4}$ ³⁻ ranging between 0.10 to 1.74 μ M.

Within the ST, the DIN concentration was low and ranged between 0.41 to 5.05 μ M (mean = 2.20 ± 0.33 μ M), SiO₄-4- ranged between 1.21 to 2.27 μ M (mean = 1.87 ± 0.28 μ M) and PO₄³⁻ ranged between 0.10 to 0.52 μ M (mean = 0.33 ± 0.07 μ M) (Figure 4.5 a,b and c). Within the SANT domain, DIN concentrations were higher than those of ST, with concentrations ranging from 8.05 to 9.65 μ M (mean= 9.02 ± 0.11 μ M) (Figure 4.5a). Chl-*a* concentrations were highly variable and ranged between 0.15 to 3.98 mg/m³. Vertical profiles show similar distributions, with slightly uniform concentrations from the surface to approximately 100 m depth (ranging between 0.03 to 2.96 mg/m³), and then decrease to lower values, with no pronounced Chl-*a* max observed, except at GT4 and SAZ2 station, where a significantly elevated Chl-*a* max was observed at about 85 and 20 m depth, respectively (Figure 4.5d).



Figure 4.5: Water column distributions of a) DIN (μ M), b) SiO₄⁻⁴ (μ M), c)PO₄³⁻ (μ M), d) Chlorophyll-*a* (mg/m³) along the South to North transect

4.1.3.2 : Southeast transect

In general, the stations along the Southeast transect exhibit similar water column distributions of macronutrients to those observed in South to North transect with uniform concentrations from the surface to approximately 120 m, followed by an increasing concentration with depth

(Figure 4.6a, b, and c; 4.8a, b, and c). Along both the MIZ East transects, macronutrients concentrations were in the similar range, with overall DIN concentrations ranged between 24.73 to 34.70 μ M (mean 29.49 ±3 μ M; n = 79), SiO₄⁴⁻ ranged from 48.11 to 116.63 μ M (mean = 82.45 ± 19 μ M; n = 79), and PO₄³⁻ ranging between 1.66 to 2.38 μ M (mean = 2.03 ± 0.2 μ M; n = 79). One of the interesting features along the MIZ south, was the elevated DIN and PO 4³⁻ concentrations and depleted SiO₄⁴⁻ concentration at MIZOA station in the upper 100 m depth (Figure 4.6a, b and c). This station was located close to the spring sea-ice, suggesting that the spring sea-ice melt probably acted as the source. Along the MIZ East, the distribution of macronutrients concentrations was highly variable, both in the upper surface and deep waters, with vertical upwelling of DIN and PO₄³⁻ from the deep waters at MIZ7 station (Figure 4.7a, b and c)



Figure 4.6: Water column distributions of a) DIN (μ M), b) PO₄³⁻ (μ M) c) SiO₄⁴⁻ (μ M), d) Chlorophyll*a* (mg/m³) along the MIZ south transect

Along both MIZ East transect, the water column distributions of Chl-*a* concentrations were lower than during South to North transect, with an overall value ranging between 0.00 to 1.71 mg/m³ (mean = 0.31 ± 0.4 mg/m³; n = 62) (Figure 4.6d and 4.7d). Interestingly, at MIZOA station, elevated Chl-a concentrations (> 0.75 contour) in the upper 150 m depth with low

values below this depth was observed This was in association with the observed enhanced DIN and PO₄³⁻ concentrations. The elevated Chl-a concentration is probably due to winter seaice melt in spring that releases trace metals such Iron (dFe) and macronutrients, which are known to facilitate phytoplankton growth (Lannuzel et al., 2016). Similarly, enhanced Chl-*a* concentration was observed at MIZ9 station in the upper surface waters (Figure 4.7d).



Figure 4.7: Water column distributions of a) DIN (μ M), b) PO₄³⁻ (μ M), c) SiO₄⁴⁻ (μ M), d) Chlorophyll*a* (mg/m³) along the MIZ East transect

4.2: Vertical profiles of DIC and TA concentrations

4.2.1 : South to North transect

The vertical profiles of DIC and TA concentrations along this transect and the mean DIC and TA concentrations in each domain are shown in Figure 4.8a, b, c and d. In general, the DIC profiles exhibit a nutrient-like behaviour, with low concentrations at the surface that increase to higher values at the subsurface depths, reaching a maximum value, then followed by a slightly decreasing but uniform DIC concentration. At most stations, TA profiles showed similar behaviour to DIC profiles in the upper surface, except at GT7B, GT8 and GT9 stations, where concentrations were elevated at near the surface, decreased to lower values at the subsurface, followed by 'slightly' increasing concentrations with depth (Figure 4.8b). In general, the water column distributions of both DIC and TA concentrations along the transect

ranged between 2079 to 2280 μ M (mean = 2182 ± 57 μ M; n = 208) and from 2262 to 2365 μ M (mean = 2307 ± 30 μ M; n = 208), respectively, with maximum gradients increasing northwards (Figure 4.8 a and b). One of the interesting features observed in the ST domain, was a high TA concentration at the surface water with concentrations of 2299 μ M (at GT8) and 2315 μ M (at GT9), that decreased to lower values of 2292 μ M (at 75 m) and 2296 μ M (at 125 m) at the subsurface water, followed by an increase in concentration with increasing depth. These low subsurface TA concentrations are due the subduction of TA- depleted AASW from the south (Figure 4.8b).



Figure 4.8: Vertical profiles of a) DIC (μ M) and b) TA (μ M) and the overall mean concentration of DIC and TA within the different domains (ANT, SANT and ST) along the South to North transect

Within the ANT domain, the DIC concentrations ranged between 2163 to 2269 μ M (mean = 2217 ± 38 μ M; n = 68), while TA was between 2283 to 2359 μ M (mean = 2318 ± 28 μ M; n = 68). In the SANT domain, both DIC and TA concentrations were slightly lower than in the ANT, with DIC values ranging between 2102 to 2259 μ M (mean = 2180 ± 53 μ M; n = 92) and TA ranging between 2261 to 2363 μ M (mean = 2302 ± 33 μ M; n = 92). The ST stations had slightly the lowest DIC concentrations than in the SANT and ANT domains, with values ranging between 2079 to 2240 μ M (mean = 2136±54 μ M; n = 37), while TA concentrations did not show any significant difference to those in the SANT, with values ranging between 2280 to 2365 μ M (mean = 2306 ± 19 μ M; n = 37).

4.3: Southeast transect

The vertical profiles of DIC and TA concentrations along both MIZ East and South transects are shown in Figure 4.9 a and b and Figure 4.10a and b. In general, the DIC and TA profiles were slightly uniform from surface to about 100 m depth, followed by an increase with depth, reaching maximum gradient at about 150 to 210 m. Below this depth, the DIC concentration decreases slightly, but uniformly, to lower value with depth, while TA increases slightly with depth (Figures 4.9 and 4.10).



Figure 4.9: Vertical profiles of a) DIC (μM) and b) TA (μM) along the MIZ south transect from MIZ0A to MIZ3

Along the MIZ south (Figure 4.10), the concentrations for both DIC and TA were lower than the other stations. In general, the DIC concentration ranged between 2169.21 to 2274.83 μ M

(mean = 2228.47 ± 33 μ M; n = 35), while TA was between 2236.51 to 2356.54 μ M (mean = 2325.73 ± 25 μ M; n = 35). During MIZ East, the DIC concentration ranged between 2185.08 to 2279.95 (mean = 2240.28 ± 30; n = 56) and TA was between 2290.90 to 2355.30 μ M (mean = 2334.05 ± 18 μ M; n = 56).



Figure 4.10: Vertical profiles of a) DIC (μ M) and b) TA (μ M) along the MIZ East transect from MIZ4 to MIZ9

4.3.1 : Distributions of DIC and TA concentrations within different water masses

4.3.1.1 : South to North transect

The water column distributions of DIC and TA concentrations are shown in Figure 4.11. Along the transect, in general, high DIC and TA concentrations signals were observed within the AABW from the south (contour of 2250 μ M for DIC and 2350 μ M for TA) (Figure 4.11a and b). The ventilation of this deep DIC-rich waters moves northwards, and concentrations becomes less pronounced within the 2225 μ M contour of the UCDW and LCDW, in association with low DO values (< 175 μ M; Figure 4.4a), high AOU concentrations (> 150 μ M; Figure 4.4b), high PO₄³⁻ values (> 2.0 μ M; Figure 4.6c) and high DIN (> 30 μ M; Figure 4.6a). Latitudinal distributions of DIC concentrations in the upper surface waters at approximately 500 m layer showed a contrast between ST, SANT, and ANT domains, with stations located in the ST, SANT exhibiting low values (ranging between 2100 to 2125 μ M) compared to the ANT stations (with values ranging between 2150 to 2225 μ M). In the deep waters (at depth > 500 m), high DIC variability was observed, with a mean concentration of 2247.5 ± 10 μ M in the ANT and

2216.2 \pm 5 μ M in the ST and SANT domain. In the ST domain, high TA concentrations were observed in the upper SSTW (mean = 2307.55 \pm 9 μ M), which decreases to lower values in the SAMW, followed by increasing concentrations in the AAIW and NADW (Figure 4.11b).





Figure 4.11: plots of a and b) water column distributions of DIC (μ M) and TA (μ M) concentrations along North to South transect

4.3.1.2 : Southeast

The water column distributions of DIC and TA concentrations along MIZ south and MIZ east (MIZ0A to MIZ3 and MIZ4 to MIZ9) are shown in Figure 4.12. Along this transect, the DIC and TA concentrations ranged between 2169.2 to 2274.8 μ M (mean = 2228.5 ± 33 μ M; n = 35) and from 2236.5 to 2356.5 μ M (mean = 2325.7 ± 25 μ M; n = 35). The DIC and TA

concentrations were significantly lower at the MIZOA station compared to MIZ1B, MIZ2, and MIZ3 stations (ANOVA, p > 0.05). At MIZ0A stations, the DIC and TA concentrations within the upper surface waters of the AASW were low and slightly uniform from near the surface to 200 m depth, with values ranging between 2169.2 to 2176.4 μ M (mean = 2173.7 ± 3 μ M; n = 5) and 2297.4 to 2299.1 μ M (mean = 2298.5 ± 1 μ M; n = 5), respectively. Below this water mass, DIC and TA values ranging between 2181.2 to 2242.5 μ M (mean = 2210.6 ± 30 μ M; n = 15) and 2297.6 to 2328.6 μ M (mean = 2311.1 ± 14 μ M; n = 15), respectively, and remained slightly uniform at greater depths within the LCDW and AABW (depth > 500 m; DIC mean = 2242.7 \pm 6 μ M and TA 2348.9 \pm 5 μ M; n = 4). Further south at MIZ1B to MIZ3 stations, we observed slightly higher DIC concentrations within the upper surface waters (at a depth between near the surface to 100 m) resulting from the winter ice melt (defined as the winter waters; WW) with values ranging between 2210.2 to 2225.4 μ M (mean = 2218.2 ± 5 μ M; n = 10). At greater depths within the LCDW (density = 27.8 kg/m^3) and AABW, the concentrations increased with depth, reaching a maximum of about 2274.3 μ M (at MIZ1B and MIZ2 stations), followed by a decreasing value to about 2255.4 μ M (DIC mean = 2261.1 ± 14 μ M and TA mean = 2349.2 \pm 11 μ M; n = 9). The TA concentrations exhibited similar distributions to DIC at these stations. One of the interesting features was a peak of low TA concentration (2236.5 µM; depth = 200 m) at MIZ2, resulting from winter ice melt.

Similarly, at MIZ4 and MIZ5 low DIC and TA concentrations were observed (DIC ranging between 2214.1 to 2232.3 μ M, mean = 2221.6 ± 6 μ M; TA ranging between 2316.6 to 2324.5 μ M, mean = 2319.3 ± 2 μ M; n = 8) within the upper surface winter waters (WW; depths from near the surface to 100 m), followed by an increase in concentrations within the UCDW (depth between 150 to 350 m; DIC mean = 2265.9 ± 11 μ M and TA mean = 2342.6 ± 7 μ M; n = 6), reaching maximum of 2278.7 and 2355.2 μ M (MIZ5) in the LCDW (depth between 175 to 250 m) and then decreases again to lower DIC value of 2260.3 μ M (MIZ5) at greater depth in the AABW (DIC mean = 2272.6 ± 9 μ M and TA mean = 2352.1 ± 2 μ M; n = 8). At MIZ6 to MIZ9, the DIC concentrations in the AASW (ranging between 2185.1 to 2200.9 μ M; mean = 2193.9 ± 5 μ M; n = 11) were lower than at MIZ4 and MIZ5 (Figure 4.12). The highest DIC and TA concentrations were observed within the LCDW and AABW, with values ranging between 2249.2 to 2273.2 μ M (mean = 2261.2 ± 8 μ M; n = 14).



Figure 4.12: plots of a and b) water column distributions of DIC (μ M) and TA (μ M) concentrations for MIZ4 to MIZ9 stations, and c and d) for MIZ0A to MIZ2 stations

4.3.1.3 : Distributions of DIC and TA concentrations in different domains along Leg2 transect

4.3.1.3.1 : The ST domain

It must be noted that the GT8 station was sampled from near the surface to 500 m depth, while GT9 was sampled near the bottom (5000 m depth, Figure 4.13), and the water mass distributions of DIC and TA were mostly characterized at the GT9 station. The DIC concentrations in this domain ranged from 2079.2 to 2239.6 μ M (mean = 2135.8 ± 54 μ M; n = 37), while TA values ranged between 2280.2 to 2364.7 μ M (mean = 2306.7 ± 19 μ M; n = 37). The lowest DIC mean concentration was observed within the upper surface waters of STSW (2104 ± 22 μ M), SAMW (2164 ± 13 μ M), and the highest mean values in the AAIW (2208 ± 29 μ M), NADW (2219 ± 11 μ M) and AABW (2238 ± 2 μ M). The mean TA concentrations were enhanced at the upper surface waters (STSW = 2301 ± 8 μ M), decreases to lower values at the subsurface waters (SAMW = 2285 ± 5 μ M), then increase again within the AAIW (mean = 2302 ± 21 μ M) and was highest in the NADW and AABW (mean = 2333 ± 5 μ M and 2360 ± 7 μ M), respectively.



Figure 4.13: Vertical profile of a) DIC (μ M) and b) TA (μ M) in the ST domain showing different water masses sampled.

4.3.1.3.2 : The SANT domain

The DIC and TA concentrations ranged between 2101.8 to 2256.8 μ M (mean = 2179.8 ± 53 μ M; n = 92) and from 2261.2 to 2362.7 μ M (mean = 2301.5 ± 33 μ M; n = 92), respectively (Figure 4.14). In this domain, the subduction of AASW resulted in the formation of AAIW (depth between near the surface to 750 m) and the DIC and TA mean concentrations in this water mass were low at 2137.4 ± 23 and 2276.1 ± 10 μ M, respectively. At greater depths, the DIC and TA concentrations were high and slightly uniform, with mean values of 2224.5 ± 23 μ M and 2310.3 ± 17 μ M within the UCDW (depth between 300 to 1250 m), respectively, and were

at 2236.4 ± 6 and 2341.5 ± 5 μ M within the LCDW (depth between 1000 and 3000 m) and were about 2248.4 ± 5 and 2357.6 ± 4 μ M within the AABW (depth > 3000 m). No significant differences were observed between the DIC and TA mean concentrations in these deep-water masses (ANOVA, p < 0.05).



Figure 4.14: Vertical profile of a) DIC (μ M) and b) TA (μ M) in the SANT domain showing different water masses sampled

4.3.1.3.3 : The ANT domain

It must be noted that the PUZ station was sampled from near the surface to 1000 m depth, (Figure 4.15a and b). In this ocean domain, the water column distributions of DIC and TA concentrations ranged between 2162.9 to 2269.1 μ M (mean = 2217.2 ± 38 μ M; n = 68) and from 2282.5 to 2359.4 μ M (mean = 2318.3 ± 28 μ M; n = 68), respectively. The depth of the AASW observed in this domain ranged between 74 to 150 m. The DIC and TA concentrations in this water mass were slightly uniform and low with mean values of 2176.4 ± 13 and 2291.7 \pm 7 μ M (n = 28). Below the AASW, we observed the shoaling tongues of the UCDW (density = 27.6 kg/m³) at depths between 98 to 1000 m, and the LCDW (density = 27.8 kg/m³) at depths between 751 to 2000 m. Within these water masses, we observed an increase in both DIC and TA concentrations with depths (Figures 4.15a and b), resulting in slightly lower mean values of 2238.4 \pm 24 μ M and 2322.5 \pm 22 μ M (n = 22) in the UCDW compared to 2252.1 \pm 8 and 2351.7 \pm 4 μ M (n = 10) in the LCDW, respectively. At greater depths (>1750 m to near the sea floor), the deep, very cold, high saline, and more dense waters of the AABW carried the slightly uniform but increasing DIC and TA concentrations, with mean concentrations of 2257.2 \pm 7 and 2356.2 \pm 2 μ M (n = 7), respectively. There was no statistically significant difference between the mean values observed in the LCDW and the AABW (ANOVA, p > 0.05).



Figure 4.15: Vertical profile of a) DIC (μ M) and b) TA (μ M) in the ANT domain showing different water masses sampled.

4.4. Mixed layer depth

Along this transect, the mixed layer depth shoal northwards, and was located deep in the ANT domain (ranging between 51.5 m at GT1 to 167.4 m depth at PUZ), shallower in the SANT (ranging between 17.9 m at GT7B to 98.2 m depth at SAZ2) and was shallow in the ST domain (32.8 at GT8 and 42.7 m at GT9) (Figure 4.16).



Figure 16: Bar plot of the mixed layer depth along the transect and per Southern Ocean domain

4.4: Correlation of DIC and TA vs $NO_{3^{2-}}$, SiO₄⁴⁻, PO₄³⁻, NO₂, Temperature, Salinity, Density, Oxygen, AOU in different domains and waters masses

The correlation coefficient between DIC and TA (main variables) with other biogeochemical parameters (temperature, salinity, density, oxygen, AOU, and macronutrients) within different domains (Antarctic and Subantarctic) and water masses are shown in Figures 4.17a, b, c and d and Figure 4.18e, f, g, and h. In this section, the ST domain was not included as it only had two stations. The dataset was binned into different water masses to understand which water mass controls the distribution of the main variables. The correlation coefficient was characterized according to the following: values above 80% were considered a strong positive correlation, values lower than -80% were considered a strong negative correlation, values below 80% were considered positive weak correlations, values greater than -80% were considered negative weak correlation (Middelburg and Middelburg, 2019).



Figure 4.17: Correlation of DIC and TA vs, NO₃²⁻, SiO₄⁻, PO₄³⁻, NO₂⁻, Potential Temp, salinity, Density, Oxygen, AOU in the Antarctic domain within a) AABW, b) AASW, c) UCDW, and d) LCDW



Figure 4.18: Correlation of DIC and TA vs DIN, NQ_3^{2-} , SiQ_4^{4-} , PQ_4^{3-} , NQ_2^{-} , Potential Temp, salinity, Density, Oxygen, AOU in the Subantarctic domain within e) AABW_SANT, f) AAIW_SANT, g) UCDW_SANT, and h) LCDW_SANT

Within the ANT, the UCDW showed that TA, and DIC had a strong positive correlation with salinity and silicate of 100 and 90% respectively. The UCDW accounted for a strong positive correlation of 80% for TA and DIC vs AOU. The other (temperature, phosphate, nitrate, nitrite) parameters on the UCDW had a weak correlation with TA and DIC. In the LCDW, all the parameters had a weak correlation with both TA and DIC. The AABW showed a strong positive correlation of 80% between TA and oxygen. Within the AASW, both TA and DIC had a strong

correlation of 90% with salinity and silicate, respectively. In this water mass, TA and DIC had weak positive correlations of 60 and 50% with AOU, respectively.

Within the SANT domain, the AABW phosphate and nitrite had a positive weak correlation of 50 and 60% with TA; for silicate and TA in the water mass, there was a strong positive correlation of 80%. In the UCDW there was a strong positive correlation of 100%, 80%, and 90% between salinity, AOU, and silicate with TA and DIC, respectively. Meanwhile, there were weak positive correlations between phosphate (60%) and nitrate (40 and 50%) with TA and DIC, respectively. At the LCDW silicate had a strong positive correlation of 80% with TA and a weak positive correlation of 50% with DIC; AOU, phosphate, and nitrate had a weak positive correlation of 40% with DIC.

4.5: Physical and biological controls of carbonate chemistry

The direction and circulation of the water masses (Figure 2.10) and the DIC and TA concentrations (Figures 4.11 and 4.19) show various processes that control the distributions of DIC, and TA should give a clear understanding of how the carbonate system behaves across the domains.

The strength of the effects and direction of different drivers of the change of DIC and TA are schematically summarized in Figure 4.19. The DIC and TA contents are additionally a function of biological (e.g., photosynthesis, respiration, and remineralization) and chemical (e.g., CaCO₃ dissolution and precipitation) processes (Zeebe and Wolf-Gladrow, 2001). To be able to study the role of biogeochemical processes on DIC and TA content, it is useful to separate the effect of physical processes, such as dilution and mixing of different water masses, from the rest. This can be done by normalizing the DIC and TA values to the salinity, which was done here according to the method by Friis et al., (2003).

The relationship between salinity normalized DIC and TA is shown in Figure 4.19. The data was split into three domains (the ST, SANT, and ANT domains). The mean of both DIC and TA of all the datasets along the transect was taken as the reference point to quantify the biochemical drivers of the carbonate system. The distribution of DIC and TA concentrations was characterized based on water mass distribution for all the stations along the transect (Figure 4.11a and b) and within the different domains (Figure 4.19a, b, and c).



Figure 4.19: Relationship between salinity normalized DIC (C_T) versus TA (A_T) in different water masses within the ST domain (a), the SANT (b), and ANT(c), and for all the dataset (d) along the transect. The water mass is identified as the AAIW, NADW, UCDW, LCDW, AABW, SAMW, STSW and AASW. The arrows indicate the impacts of the mentioned processes on the DIC concentration and the TA

Chapter 5: Discussion

Most studies of carbonate chemistry in the Southern Ocean have been undertaken during the summer months. For example, González-Dávila et al., (2011) described the carbonate system in the water masses of the Southeast Atlantic sector of the SO during February and March 2008. However, this study was designed to characterize the carbonate chemistry variables (DIC and TA) across different ACC domains and the marginal ice zone in the SO and address the spring-time observational gaps. This helps to characterize the carbonate chemistry variability in this season and close the gap in the seasonal cycle. The focus was to evaluate the physical and biological processes that control the characteristics of the carbonate chemistry across different SO domains.

Generally, the vertical and horizontal distribution of DIC and TA in the different domains is a result of the biological and physical carbon pumps. Water mass transformation and circulation is a fundamental component of ocean's thermodynamics and biogeochemistry and plays an important role in the distribution of the carbonate system in the SO. This study shows that the upwelling of the UCDW with high DIC (Figure 4.11) and AOU (Figure 4.3) associated with low nutrients (Figure 4.5) plays an important role in distributing carbon and nutrients to the upper layer of the SO. This upwelling carbon-rich UCDW enhances the carbon content of the AAIW and SAMW. A band of AAIW located between 600-1000 m depths (Figure 4.11) transports elevated DIC waters northwards. According to González-Dávila et al., (2011), the core of the AAIW moves into the Cape Basin, where it meets with the AAIW from the Indian Ocean injected with the Agulhas Rings. Above the AAIW lies the SAMW, which upwells in the Southern Benguela (Lamont et al., 2015; Siddigui et al., 2023) with elevated DIC and less TA, but DIC slightly less than the AAIW (Figure 4.11). According to Siddigui et al., (2023), the transport of water masses from the SO across the South Atlantic shapes the characteristics of the upwelling source water masses of the Benguela Upwelling System. This highlights the importance of understanding changes in the SO related to CO₂ dynamics and the coupling between the SO and the Benguela Upwelling System.

5.1: Processes that control DIC and TA distribution in the different SO domains

To identify processes affecting DIC and TA concentration in spring, I examined the physical and biological mechanisms underlying the distribution in different water masses of the Subtropical, Subantarctic, and Antarctic domains.

5.1.1 : Subtropical (ST) domain

Figure 4.19a shows that within the ST domain the processes that drive the carbonate chemistry include photosynthesis, CO₂ release, and CaCO₃ dissolution. In this domain, high surface (STSW) temperatures with low DIC concentrations were observed as compared to the ANT domain, which lies at the higher latitudes. This agrees with Wu et al., (2019) and Cai et al., (2020), who emphasized the importance of the solubility pump. This relies on the assumption that higher latitudes have greater DIC concentrations because CO 2 solubility is increased in waters with lower temperatures. It is highly unlikely that the release of CO₂ dominated the surface waters. The high concentrations of chlorophyll-a in the surface waters of this domain also indicate that photosynthesis was taking place in this region. When photosynthesis occurs, CO2 and nutrients are consumed, which lowers the concentration of DIC in surface waters. According to Zeebe and Wolf-Gladrow, (2001), DIC decreases and TA increases slightly in the water column during photosynthesis because of nitrate and hydrogen ion consumption when proteins are formed. Hence, the presence of low DIC and nutrients concentrations within this domain indicates that photosynthesis was taking place. The high DIC and TA observed below 1000 m depth in the AAIW, NADW, and the AABW (Figure 4.11) was most likely due to the dissolution of CaCO₃. As shown in Figure 4.19a, CaCO₃ dissolution increased DIC and TA in deep waters in this domain. In the deep ocean, dissolution of CaCO₃ occurs to increase DIC and TA through the release of $CO_{3^{2-}}$ (Daniels, 2015).

5.1.2 : Subantarctic (SANT) domain

In the SANT domain, similar dominant processes were observed as in the ANT domain except that the different processes happen in different water masses. Dissolution of CaCO ₃ was a dominant process in deep waters (NADW, UCDW, LCDW, and AABW). CO₂ was released in the surface water (AASW) while CaCO₃ precipitation was also taking place in the surface and intermediate waters (AAIW). The process of respiration controlled the carbonate dynamics within the intermediate waters (AAIW) and the upper deep waters (UCDW).

In the spring, the Subantarctic domain experiences:

1. Higher surface temperatures: Warmer seas cause CO_2 to become less soluble, which encourages its emission (CO_2 release) (Cai et al., 2020).

2. Enhanced biological activity: As phytoplankton production and growth rise, more CO ₂ is taken up by photosynthesis, but there is also a rise in respiration below the euphotic layer, which releases CO₂ in deep waters (Buesseler et al., 1998).

3. Upwelling and ventilation: When deep waters rich in carbon rise to the surface due to winddriven upwelling and ventilation events, CO₂ is released to the atmosphere (Sarmiento et al., 2004).

4. Sea ice melting: As sea ice melts, freshwater is added, which dilutes seawater and reduces the pH and the concentration of CaCO₃. Low carbonate ion concentration may result in low buffering capacity, which is the ability to neutralize CO₂ (Arrigo, 2014).

5.1.3 : Antarctic (ANT) domain

In this region, high DIC associated with high nutrients extended to the surface waters (AASW) from the bottom (Figure 4.5). However, Figure 4.19c shows no evidence of the exchange of CO₂ gas between the atmosphere and the ocean, which could be attributed to the presence of sea ice. Sea ice inhibits CO₂ outgassing by acting as a barrier to air-sea exchange and reduces biological uptake by blocking the penetration of light to the ocean surface (Gupta et al., 2020). The stations along the Marginal Ice Zone (Figure 4.12) show high DIC exceeding 2250 µM occupying subsurface waters below 100 m depth. The Chlorophyll-a concentrations increased in the surface waters (0-150m) from GT2B to GT3 and became higher when reaching the APF, this trend is the same for the DIN concentrations. This indicates that upwelling nutrient-rich deep waters fuels productivity in this region. Most of the dataset indicates that CaCO₃ dissolution and precipitation were the dominant processes that controlled the carbonate dynamics. Figure 4.19c shows that the CaCO₃ dissolution was dominant in the deep waters (NADW, LCDW, and UCDW), while precipitation was a dominant process in the intermediate waters (AAIW). The formation and dissolution of CaCO₃ changes DIC to TA ratio by 2:1 (Zeebe and Wolf-Gladrow, 2001). The DIC and TA reduction due to CaCO₃ precipitation observed in the AAIW precipitation was less pronounced compared to the dissolution.

Conclusion

This study contributes towards understanding the carbonate chemistry patterns and driving processes in the Southern Ocean that will help to assess the role it plays in regulating anthropogenic CO2. The results demonstrated that there are differences in the carbonate system levels across the different fronts; they also show different concentrations of carbonate chemistry variables across the different water masses. While biological processes significantly change the carbonate chemistry properties in each domain, water mass circulation transports DIC and TA across the SO sector into the low latitudes. Panassa et al., (2018) estimated that 75% of the DIC change in the AAIW, which constitutes an important mechanism for the transport of DIC and macronutrients out of the SO into the low latitudes, has an anthropogenic origin. Since the SO waters influence upwelling waters in the Benguela Upwelling system, changes in the carbonate system due to the uptake of the anthropogenic CO2 may increase DIC in upwelling waters of the Benguela Upwelling System. Such an increase in upwelling DIC may increase the vulnerability of the Benguela Upwelling System to ocean acidification. Therefore, in addition to understanding the distribution and processes governing the carbonate system in different seasons, this study further highlights the need to understand the coupling of the SO to the Benguela Upwelling System and the impacts that changes in the upwelling source waters may have on the ecosystem.
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