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Robyn Elizabeth Tuerena
Nitrogen and carbon cycling in the South Atlantic Ocean: A stable isotope study along a 40°S transect (UK GEOTRACES)

Robyn E. Tuerena

Thesis submitted for the degree of Doctor of Philosophy
The University of Edinburgh
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Acronyms

AABW = Antarctic Bottom Water (=LCDW + WSDW)

AAIW= Antarctic Intermediate Water

AASW = Antarctic Surface Water

AC = Agulhas Current

ACC = Antarctic Circumpolar Current

BC = Brazil Current

BMC = Brazil-Malvinas Current

CDW = Circumpolar Deep Water

ETNP = Eastern Tropical North Pacific

ETSP = Eastern Tropical South Pacific

LCDW = Lower Circumpolar Deep Water

MC = Malvinas Current

MOC = Meridional Overturning Circulation

MOW = Mediterranean Overflow Water

NADW = North Atlantic Deep Water

ODZ = Oxygen Deficient Zone

PAZ = Polar Antarctic Zone

PDW = Pacific Deep Water

SACW = South Atlantic Central Water
SAF = Subantarctic Front
SAMW = Subantarctic Mode Water
SASW = Subantarctic Surface Water
SAZ = Subantarctic Zone
SSIZ = Seasonal Sea Ice Zone
SSTC = South Subtropical Convergence
UCDW = Upper Circumpolar Deep Water
WSDW = Weddell Sea Deep Water
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Abstract

Fixed N (nitrate, nitrite, and ammonium) is a limiting nutrient for photosynthesis in the surface ocean. The rates and relative importance of N cycling processes, however, are temporally and spatially complex, which hamper their direct measurement and quantification. The South Atlantic subtropical front separates the Atlantic Ocean and the subantarctic, an area which can elucidate information about water masses both entering and leaving the basin. Through the GEOTRACES programme, an oceanographic section across 40°S in the South Atlantic is used to investigate biogeochemical cycling of nitrogen and carbon in this region. Hydrographic data, in combination with the isotopic composition of nitrate (NO$_3^-$), particulate organic carbon and particulate nitrogen ($\delta^{15}$N$_{POC}$, $\delta^{18}$O$_{NO3}$, $\delta^{13}$C$_{POC}$, $\delta^{15}$N$_{PN}$), is used to provide integrative measurements for temporally and spatially variable processes of the marine N-cycle and C-cycle.

A thorough examination of the stable isotope cycling of particulate and dissolved N across the subtropical front is used to quantify the supply of fixed N to the mixed layer. The relative importance of nitrate from the subsurface, N$_2$ fixation, terrestrial input and atmospheric deposition in supplying production is determined. Typically, 30-50% of the export flux in the subtropical water masses is sourced from N$_2$ fixers and up to 75% within the Brazil Current. This finding suggests that diazotrophs may be abundant in the South West Atlantic providing a source of new N to this region. To assess the basin scale N-cycling processes, the deep water masses were analysed to reveal the origin and history of NO$_3^-$. Intermediate waters formed in the subantarctic are enriched in $\delta^{15}$N$_{NO3}$ and $\delta^{18}$O$_{NO3}$ from partial utilisation by algae. This enrichment in $\delta^{15}$N$_{NO3}$ is not present in the subtropical North Atlantic or the return flow of the North Atlantic Deep Water (NADW), which decreases from ~5.9‰ in the newly formed intermediate waters to ~4.8‰ in the NADW at 40°S. The modification of isotopic signatures through the subtropical Atlantic can be calculated as an incorporation of 26-36 Tg N yr$^{-1}$ of newly fixed N from an isotopic source of -1‰ (N$_2$ fixation). The extent of N addition is higher than estimated rates of N loss within the Atlantic and surpasses the amount of N deficit supplied to the basin.
Fixed N inputs and losses through the global ocean are investigated by the assessment of remineralised nitrate added to the ocean interior. A lower $\delta^{15}\text{N}$ is observed in Atlantic remineralised nitrate in comparison to the Pacific. The relative importance of N$_2$ fixation and pelagic denitrification within each ocean basin is quantified and through this approach, N$_2$ fixation rates are estimated at 92-116 Tg N yr$^{-1}$ in the Pacific and 24-32 Tg N yr$^{-1}$ in the Indian Ocean. Combining Atlantic N$_2$ fixation of ~32 Tg N yr$^{-1}$ with Indo-Pacific, global N$_2$ fixation rates can be estimated at 142-184 Tg N yr$^{-1}$. The high inputs in the Pacific suggest that excess P is the dominant control on the success of N$_2$ fixers. However, estimates of new N addition to the Atlantic indicate other mechanisms such as the recycling efficiency of P and supply of Fe to the surface ocean increase N$_2$ fixation rates above this threshold.

The organic matter supplied to sediments is principally derived from phytoplankton across the subtropical front. High organic content is associated with the productive Brazil-Malvinas Confluence region where a diverse supply of nutrients sustains elevated biomass. The Rio Plata outflow is characterised with high $\delta^{15}\text{N}_{\text{NO3}}$ and $\delta^{15}\text{N}_{\text{PN}}$, suggesting denitrification processes occur in the estuary. A low $\delta^{13}\text{C}$ source associated with high Al concentrations is identified on the western slope, indicating a supply of terrestrial derived C to the deep ocean. The fractionation of C uptake by phytoplankton is assessed in subtropical and subantarctic waters. In the subantarctic, CO$_2$[aq] and growth rates determine the extent of C isotope fractionation. In this region, low species diversity and a small range in cell size enable the fractionation from CO$_2$[aq] and growth rate to be expressed in phytoplankton. In subtropical water masses a larger range of cell size is the principal determinant of C fractionation. Increased surface area to volume is the main mechanism for increasing C uptake, arguing against the use of $\delta^{13}\text{C}_{\text{POC}}$ as a palaeoproxy. The low $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{PN}}$ observed in the subtropics (from C fractionation and N$_2$ fixation) contrast the heavier signatures in the subantarctic. These observations are propagated to the sediments, wherein organic matter shifts are determined by changes in the subtropical front over time. The results of this study have greatly improved knowledge of N and C cycling within the South Atlantic, providing new insight into the cycling of these two important elements in the surface and deep ocean, on a regional and global scale.
Approximately half of global photosynthesis occurs in the ocean, mainly carried out by algae which grow in surface waters. Across most of the global ocean their growth is limited by the low concentrations of the nutrient, nitrogen, in surface waters.

Humans are currently altering the natural nitrogen cycle at an unprecedented rate. Fertilizer production and combustion processes are increasing the inputs of nitrogen to the ocean. In addition, ocean warming may increase ocean deoxygenation and the rate at which nitrogen is lost from the ocean. These changes may significantly alter marine ecosystems.

The natural perturbations in the marine nitrogen cycle (loss and gain) may be internally regulated by negative feedbacks, and could play an important role in regulating human induced changes. For example, the growth of algae which fix nitrogen from the atmosphere can combat losses of nitrogen from low oxygen environments.

As it takes approximately 1000 years for the waters within the ocean to fully circulate, unless these negative feedbacks occur locally, human induced changes may significantly alter the amount of nitrogen held within the oceans. The stronger the negative feedbacks, the more likely the oceans are to modulate the impacts of human activity.

This thesis examines the balance between nitrogen loss and gain from the Atlantic Ocean to understand its role within the global ocean system. This helps to greater understand the internal regulation of the marine nitrogen cycle. This knowledge may be used to determine the implications of human perturbations on the health of the global ocean.
1 Introduction

Carbon (C) and nitrogen (N) are two of the most important elements for life and their cycling in the ocean influence marine productivity. This study investigates the biogeochemical cycles of these elements in the South Atlantic Ocean.

1.1 An introduction to the marine nitrogen cycle

Fixed N is a vital nutrient for the growth of phytoplankton in the surface ocean. In most oceanic regions, fixed N is fully consumed and limits primary production. As such the amount of fixed N available to phytoplankton affects marine productivity and plays a central role in the control of marine biogeochemistry. There are many forms of N within the ocean, although the most abundant, N\textsubscript{2}, is not bioavailable for the majority of photosynthetic organisms. All other forms are classed as fixed N as they are bioavailable for uptake by primary producers. The unavailability of N\textsubscript{2} gives significance to the process of N\textsubscript{2} fixation in which N\textsubscript{2} is converted to organic matter by the growth of diazotrophs (N\textsubscript{2} fixing species). N\textsubscript{2} fixation and N loss (anammox and denitrification) are the dominant processes which affect the size of the marine fixed N inventory and thus the extent of marine productivity. The temporal and spatial variability of these processes coupled to the physical circulation of ocean waters determines the extent of biological production within the ocean. The principal form of fixed N within the ocean is as nitrate (NO\textsubscript{3}\textsuperscript{-}), which accounts for ~88% of the marine N reservoir (Gruber, 2004).

Biological production, which converts inorganic carbon and nutrients to organic matter, occurs in the sunlit surface ocean. The majority of this organic matter is remineralised (or nitrified) back into dissolved N species within the euphotic zone, but a small proportion of organic matter is exported to the subsurface. Through the process of biological fixed-N uptake and organic matter export, there is an accumulation of NO\textsubscript{3} with depth and a depletion of NO\textsubscript{3} within surface waters. To account for the loss of fixed N from the surface, NO\textsubscript{3} is resupplied by ocean circulation, providing necessary nutrients to the sunlit waters. This biological and physical transportation determines the distribution of most of the elements in the ocean. The “loop” of biological production, export and physical resupply is one of
the dominant processes which regulate the amount of CO$_2$ within the atmosphere (Figure 1.1). A higher efficiency of biological export of nutrients would draw down more CO$_2$ from the surface ocean and thus lower atmospheric CO$_2$. Greater marine productivity has been hypothesised as one of the principal explanations for glacial/interglacial changes in CO$_2$ concentrations in addition to orbital forcing.

![Figure 1.1 An overview of the main processes within the marine nitrogen cycle and interactions with the cycles of carbon, phosphorous and oxygen. Fixed N is cycled internally within the ocean via a number of redox and recycling processes. Fixed N that is supplied to the euphotic zone is rapidly consumed by phytoplankton except in regions where other nutrients or light are limiting production. Fixed N is lost from the marine system via anammox and denitrification and burial with sediments. New N is added to the ocean via rivers, atmospheric deposition and N$_2$ fixation. Taken from Gruber, (2004).](image)

### 1.1.1 N$_2$ fixation

During N$_2$ fixation, N$_2$ is reduced to ammonia, which is utilised for production and growth. This reaction is catalysed by the nitrogenase enzyme which is dependent on Fe availability (Paerl et al., 1994). In addition, diazotrophs are reliant on a supply of P for metabolic reactions, with an excess of P over N favouring the growth of N$_2$ fixers (Deutsch et al., 2007). In the earliest work into the importance of diazotrophs it was thought that *Trichodesmium* abundance accounted for the vast majority of N$_2$
fixation (Carpenter et al., 1983). However in recent years, the importance of other groups of diazotrophs has emerged (Sohm et al., 2011). From a biogeochemical perspective it is crucial to understand the spatial distribution of N\textsubscript{2} fixers to determine the coupling of N inputs and losses from the ocean.

Different cyanobacterial groups have different distributions and ecological niches within the ocean (Sohm et al., 2011; Zehr, 2011). In the warm subtropical gyres, the filamentous cyanobacteria *Trichodesmium* are common, which form easily observable colonies. It has been suggested that the abundance of individual trichomes may exceed colonies although this is still disputed (Orcutt et al., 2001; Gonzalez Taboada et al., 2010). *Trichodesmium* have gas vacuoles which can be used to control buoyancy (Capone et al., 1997). A daily cycle of rising and sinking in the water column, likely a result of increases in dense carbohydrates/proteins through the day, allows optimisation of light availability and nutrient scavenging at depth (in particular phosphate) (Villareal and Carpenter, 2003). In addition, *Trichodesmium* have the ability to use organic phosphorous as it encodes alkaline phosphatases that are expressed under P limitation (Orchard et al., 2009). Heterocyst-forming cyanobacterial symbionts are observed in several oceanic diatom genera (Carpenter and Foster, 2002; Foster et al., 2009). Heterocysts found in association with diatom species, are known as diatom diazotroph associations (DDAs), and are widely distributed through the warm, oligotrophic ocean. The high density of silicon-walled diatoms suggest DDAs may play an important role in carbon export (Subramaniam et al., 2008). Small N\textsubscript{2} fixers (below 10 µm), which consist of unicellular diazotrophs, have only recently been observed (Zehr, 2011). There are three main groups, *Crocosphaera watsonii*, UCYN-A and UCYN-B. Unicellular bacteria have been found in a diverse range of tropical environments and when at high densities can equal or exceed *Trichodesmium* N\textsubscript{2} fixation rates (Montoya et al., 2004; Goebel et al., 2010).

*Trichodesmium* are the most abundant diazotrophs in the North Atlantic. The Pacific, however, is dominated by unicellular diazotrophs, in particular UCYN-A. *Trichodesmium* may have a selective advantage in low-P areas, due to their ability to obtain nutrients from greater depths and uptake other forms of available P.
*Trichodesmium* are more P-limited in the Atlantic compared to the North Pacific, where low Fe inhibits *Trichodesmium* and allows the dominance of UCYN-A (Sohm et al., 2008). In the central and southern gyres of the Atlantic and Pacific, there is evidence for abundant unicellular cyanobacteria (Moisander et al., 2010), although their contribution of new N to the ocean is still poorly understood. Heterocystous symbionts have a much patchier distribution as they require silicon for diatom growth; large densities are commonly observed in the Amazon plume. From the variability in species size, composition and morphology, the fate of N in different ocean basins is likely to differ geographically. The modes of export and transfer into the food web also depend on the community composition of diazotrophs (Sohm et al., 2011).

The temporal and spatial variability of species abundance highlights the need for integrative tracers to assess the relative importance of new N addition in different oceanic regions.

### 1.1.2 Atmospheric deposition

As described above, the locations and pathways in which fixed N are transferred to the ocean directly influence marine productivity. Fixed N can also be added to the ocean by atmospheric deposition of dissolved and particulate N. Wet deposition of N by rainwater includes DIN (nitrate, nitrite and ammonium) and DON. Gas phase N which contributes to dry deposition includes ammonia, nitric acid and organic N compounds. Furthermore particulate N, such as dust and organic debris, may be deposited as either dry deposition or with rainfall. In estuaries atmospheric deposition directly to the water surface can account for a significant fraction of N input (Galloway, 2004). There is a wide range in the relative magnitude of atmospheric deposition occurring in coastal and continental shelf regions, which make estimations of this process challenging. Globally anthropogenic sources of fixed N contribute ~70% of NOx and 65% of ammonium deposition (Galloway, 2004). Anthropogenic derived material is increasing through both the direct emissions of oxidized N species and NH$_3^+$ and the secondary formation of organic N (Duce et al., 2008). Water soluble organic N may be more abundant than previously
thought, accounting for approximately 30% of deposition (Jickells, 2006). Increasing amounts of atmospheric deposition from anthropogenic sources may now account for approximately one third of external N supply to the ocean, therefore significantly altering the marine N cycle (Duce et al., 2008). It is therefore important to distinguish between the role of N₂ fixation and atmospheric deposition (both natural and anthropogenic) in the marine N cycle, to further understand their effects on marine productivity.

1.1.3 Denitrification

Denitrification occurs in low O₂ environments as nitrate replaces oxygen as the terminal electron acceptor in respiration, reducing NO₃⁻ to N₂ which is unavailable to most phytoplankton. This can occur in suboxic regions of the water column or in sediments. Denitrification within the water column occurs in three main regions, the Eastern Tropical North Pacific (ETNP), Eastern Tropical South Pacific (ETSP) and the Arabian Sea (Naqvi 1987, Deutsch et al., 2001). Benthic denitrification is more evenly distributed throughout the ocean basins, but is highest on continental margins where there is a higher supply of organic material to the sediments. As N₂ fixation dominates the flow of N into the ocean, it is essential to constrain its rates in comparison to denitrification and anammox estimates (Brandes and Devol, 2002; Codispoti et al., 2001). It has been previously estimated that N loss far exceeds rates of N₂ fixation (Codispoti et al., 2001; Brandes and Devol, 2002) which would suggest the ocean is progressively losing fixed nitrogen. However geochemical evidence suggests the sources and sinks of N are relatively balanced (Deutsch et al., 2004; Gruber, 2004).

As N₂ fixation and denitrification are the main determinants of the N reservoir a decoupling of N₂ fixation and denitrification within different ocean basins could perturb the marine N inventory. Over the last 10,000 years atmospheric CO₂ concentrations have been relatively constant within 10 ppm, which suggests effective feedback mechanisms for keeping the 3000 year cycle in balance (Gruber, 2004). This is further supported by the global distribution of ocean nitrate and phosphate data which is tightly coupled to a 16:1 ratio within the ocean (Figure 1.6).
Phosphorous (P) is principally supplied to the ocean by continental weathering and has a residence time an order of magnitude higher than N. The tight coupling between N and P within the ocean suggests that there is a coupling between the two processes of N loss and gain to maintain nutrient concentrations at a 16:1 ratio (Figure 1.2, Gruber and Sarmiento, 1997).

![Figure 1.2 A global dataset of nitrate and phosphate data in the global ocean (WOCE data). The intercept of nitrate and phosphate falls close to 0, supporting a coupling between the processes of N input and N loss. A high N:P ratio (or high N*) would encourage denitrification and a low N:P ratio (or low N*) would encourage the growth of N\textsubscript{2} fixers. Adapted from Sigman and Hain, (2012).](image)

1.1.4 Anammox

Denitrification occurs concomitant with protein oxidation and the liberation of the amino group NH\textsubscript{4}\textsuperscript{+}. Without a process of NH\textsubscript{4}\textsuperscript{+} oxidation, NH\textsubscript{4}\textsuperscript{+} would accumulate in denitrification regions, however this is not observed in the oxygen deficient regions of the global ocean (Codispoti, 1973). The existence of an anammox reaction in
nature was therefore postulated before its discovery in bacteria. Anammox bacteria are chemoautotrophic bacteria which fix CO$_2$ using nitrite as an electron donor. This process removes NH$_4^+$ from the water column converting it back into N$_2$. Globally this process may be responsible for 30-50% of global oceanic N$_2$ production (Dalsgaard et al., 2005).

1.1.5 Coupling of N addition and loss

Estimation of the rates at which newly fixed N is added to the global ocean by diazotrophs have changed dramatically since research began in this field, with estimates increasing from ~1.4 Tg N yr$^{-1}$ in 1982 to ~140-180 Tg N yr$^{-1}$ (Carpenter, 1983; Deutsch et al., 2007; Grosskopf et al., 2012). As N has a relatively low residence time in the ocean (~3000 years), in comparison to phosphorous (~10,000 years) it may be susceptible to dynamic changes if there is no coupling between the processes of N addition and N loss. In recent years, estimations of the rates of the two processes have converged, perhaps with increased evaluation of the methods used to constrain them (e.g. Grosskopf et al., 2012, DeVries et al., 2012). One of the key questions still remaining is whether the two processes are coupled within ocean basins, with rapid negative feedbacks keeping the N reservoir in balance. The relative significance of phosphorous (P), iron (Fe) or both, as primary drivers for the success of N$_2$ fixers may help to determine this.

In recent years it has been suggested that the majority of N$_2$ fixation occurs in proximity to oxygen deficient zones (ODZs), which supports the view that N loss and N addition are coupled (Deutsch et al., 2007). A deficit of NO$_3^-$ (compared to PO$_4^{3-}$) is thought to inhibit the growth of non-diazotrophs and to favour the growth of N$_2$ fixers. High excess P concentrations are identified in the ETNP and ETSP, Subarctic North Pacific, Arabian Sea and off the western coast of Africa. In these regions nitrate is consumed through denitrification rendering ODZs enriched in phosphate. Using this reasoning, the areal rates of N$_2$ fixation in the Pacific would be twice as high as those in the Atlantic, hosting 2/3 of global N$_2$ fixation (Deutsch et al., 2007). This concept would suggest homeostasis within the marine N cycle with N loss promoting N$_2$ fixers by the supply of excess phosphate, and higher fixed N
promoting increased productivity and expansion of ODZs. Evidence from the Eastern Tropical South Pacific (ETSP) may support the growth of diazotrophs in these regions even with low Fe concentrations (Bonnet et al., 2013). However other studies have suggested that the N\textsubscript{2} fixation rates in the ETSP are low (Sohm et al., 2011).

If excess P is the dominant control, it would imply lower rates of N\textsubscript{2} fixation in the Atlantic than recent work suggests (Yoshikawa et al., 2013). Dissolved PO\textsubscript{4}\textsuperscript{3-} concentrations are typically 0.1-0.2 µM in most of the surface open ocean (Cavender-Bares et al., 2001; Karl et al., 2001; Moutin et al., 2008) except the North Atlantic where they can be as low as 0.001 µM in the western basin (Moutin et al., 2008). The Atlantic remains a paradox in the role it may play in global N\textsubscript{2} fixation: are rates solely determined by P supply or do other factors change this coupling? In the Atlantic Ocean, there are high Fe deposition rates and no significant N loss from ODZs, therefore the process of N\textsubscript{2} fixation within this basin may provide a net source of N to the global ocean and decouple the processes of N addition and N loss. Fe is supplied to the ocean surface via dust from desert regions and greater Fe concentrations are deposited in the northern ocean basins from closer proximity to continental land mass. The North Atlantic receives approximately ~1 nM of Fe to the surface compared to ~0.3 nM in the South Atlantic (Bergquist and Boyle, 2006; Moore et al., 2009). In the Pacific, Fe supply is typically ~0.1-0.2 nM, but higher near island archipelagos (Brown et al., 2005). Although P limits the growth of *Trichodesmium* in the North Atlantic, this species has many mechanisms which can counteract P limitation, by increasing uptake of dissolved organic phosphorous (DOP) and dissolved inorganic phosphorous (DIP) and decreasing the requirement for cellular P (Mulholland et al., 2002; Fu et al., 2005; Krauk et al., 2006). These features may argue against excess P as the ultimate limitation for diazotroph success. Increasing evidence suggests that DOP has an important role in the North Atlantic for *Trichodesmium* success (Mather et al., 2008; Lomas et al., 2010). Although the vast majority of work finds N\textsubscript{2} fixation more abundant in the North Atlantic, higher excess P concentrations in the South Atlantic may suggest higher rates than previously hypothesised (Deutsch et al., 2007). Indeed recent work has found evidence for the presence of unicellular diazotrophs in the South West Atlantic
which may suggest a higher amount of N\textsubscript{2} fixation occurring in the South Atlantic than previously anticipated (Moore et al., 2014).

Recent work suggests that Fe and P both control N\textsubscript{2} fixer abundance (Ward et al., 2013; Weber and Deutsch, 2014). It is emerging that both Fe and P are important and Fe may be locally limiting whereas P determines the overall importance of N\textsubscript{2} fixers in each basin (Weber and Deutsch, 2014). Modelling studies require further testing with integrative measurements of N\textsubscript{2} fixation supply to different regions. In addition to the current uncertainties of the natural marine N cycle, anthropogenic perturbations are likely to have a significant effect on the biogeochemical cycling of C and N. A warming climate is likely to increase the extent of ODZs within the ocean and thus may increase the extent of N loss from the ocean. In addition Fe deposition to the ocean may be reduced with changes to the climate (Mahowald et al., 2006). These processes may have a large effect on the marine N reservoir, in particular if fixation and loss are not well coupled. Humans are currently fixing as much N as the marine biosphere, having significant impacts on coastal regions and atmospheric deposition rates (Duce et al., 2008; Gruber and Galloway, 2008). These large perturbations and the current gaps in our understanding highlight the need for ongoing study of the dynamics of the marine N cycle in all regions of the ocean. The relative coupling of N fixation and loss will have implications for how the marine environment will respond to rising temperatures, reduced Fe and increased fixed N fluxes from anthropogenic changes in the future.
1.2 An introduction to the marine carbon cycle

More than 50 times as much carbon is held within the ocean in comparison to the atmospheric inventory. As such the ocean plays an important role in the modulation of the earth’s climate. Atmospheric CO$_2$ has increased from $\sim$280 ppm to $\sim$400 ppm since industrialisation in the 19th century, which is larger than glacial-interglacial perturbations of 80-100 ppm (Sigman and Boyle, 2000). The ocean modulates the effects of anthropogenic CO$_2$ by its absorption in biological and chemical processes. Phytoplankton absorb CO$_2$ through photosynthesis, providing carbon for marine ecosystems. Some of this carbon sinks through the water column, thereby decreasing CO$_2$ in the surface waters and increasing dissolved inorganic carbon (DIC) with depth. The inorganic C pool in the oceans is governed by carbonate chemistry. The majority of C is present as bicarbonate ions (HCO$_3^-$) due to the reaction of H$_2$O + CO$_2$ to H$^+$ and HCO$_3^-$, while a small amount of HCO$_3^-$ may disassociate to H$^+$ + CO$_3^{2-}$. The organic and inorganic forms of carbon are linked via the marine biological pump. Phytoplankton consume CO$_2$ or bicarbonate in surface waters, thus decreasing the inorganic carbon pool in the euphotic zone by its conversion to organic matter. Organic matter is then remineralised with a small proportion of this being exported from the euphotic zone to depths. This pumping of carbon from the surface ocean to depth drives the DIC gradient within the ocean, with low concentrations in the surface and higher concentrations at depth. This process drives a drawdown of atmospheric CO$_2$ into the surface ocean, by the equilibrium between the two CO$_2$ reservoirs.

The diversity of phytoplankton in surface waters is determined by the environmental conditions which surround them. In low nutrient subtropical regions, small cyanobacteria are dominant. These cells have a greater surface area to volume, specialised to take up nutrients at low concentrations. In polar regions where there are high concentrations of macronutrients, larger phytoplankton such as diatoms are dominant. In these conditions, phytoplankton can be abundant and produce a high proportion of sinking material. The niches of phytoplankton are determined by the surrounding biogeochemical conditions, and are likely to change with increased CO$_2$ and temperatures. It is unclear at present how different species are likely to respond.
to climate driven changes, which highlights the need to investigate the mechanisms under which they operate within the surface ocean. The relative success of different types of phytoplankton has implications for our understanding of carbon drawdown and the biological diversity of marine systems.

Coastal regions connect the continents with the open ocean, providing a significant source of carbon and nutrients. Despite this, their importance in local and global carbon budgets remains unclear, mainly due to the complexity of coastal systems. Continental shelves and slopes constitute 15-20% of ocean surface area yet these regions account for approximately 50% of ocean primary productivity and new production (Eppley and Peterson, 1979; Prahl et al., 1994). Continental margins are important for the export and transformation of organic matter from rivers to the open ocean (Hedges et al., 1997; Keil et al., 1997; Bauer et al., 2001). Through riverine input, coastal margins receive and produce an excess of organic carbon. Residual matter can be transported offshore and contribute to the productivity of the open ocean (Bauer and Druffel, 1998). The main terrestrial source of organic matter to the coastal regions are rivers, which supply on average 0.25 Pg yr$^{-1}$ of dissolved organic carbon and 0.15 x10$^{15}$ Pg yr$^{-1}$ of particulate organic carbon (Hedges et al., 1997). This particulate riverine input, however, serves as a paradox for the global carbon budget in the oceans, as they surpass values of total organic carbon buried in marine sediments (Raymond and Bauer, 2001). Determining the fate and relative contribution of terrestrial organic matter to the world’s oceans is imperative to the understanding of the biogeochemical cycling of carbon and nitrogen (Hedges et al., 1997).
1.3 An introduction to the South Atlantic

The boundary of the South Atlantic at ~40°S is a region which connects the Atlantic with the Southern, Indian and Pacific Oceans. As such it provides a unique region for investigating N and C cycling processes. The southward flow of the North Atlantic Deep Water (NADW) is compensated by the northward flow of Southern Ocean intermediate and bottom waters. A transect of the South Atlantic allows the deep and surface water masses to be studied to identify their importance in N cycling processes on a local, basin-wide and global scale. The subtropical convergence is a region where contrasting biogeochemical regimes meet, and provides an opportunity for the changes in N and C cycling processes and their impacts on phytoplankton to be investigated.

1.3.1 Surface water masses of the South Atlantic

The South subtropical convergence that lies at approximately 40°S marks the boundary between the oligotrophic subtropical gyres and the Southern Ocean. The low- and high-macronutrient regimes converge creating a dynamic nutrient environment which fuels enhanced productivity in these regions. The enhanced chlorophyll concentrations have been hypothesized to be a result of nitrate- and Fe-limited waters converging, providing the nutrients to support the further growth of phytoplankton (Ito et al., 2005; Browning et al., 2014). It has also been suggested that increased thermal stability of the water column is provided from subtropical waters which allows a higher availability of light for phytoplankton growth (Llido et al., 2005). This environment is difficult to characterize due to the complex nature of water mass transport, but it provides a unique region where subtropical and subantarctic waters can be studied simultaneously.

The subtropical waters within the South Atlantic are principally the South Atlantic Central Water (SACW) and Brazil Current sourced in the Atlantic, and the Agulhas leakage which is supplied to the Atlantic via South East Africa (Figure 1.3). The subtropical water masses are all characterized with high salinities and low nitrate concentrations. The SACW exhibits a linear temperature-salinity relationship, with typical properties of 5-20 °C and 34.3- 36 psu (Stramma and England, 1999). This
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Layer of uniform density is subducted into the thermocline during winter as a deep surface layer of uniform temperature and salinity. The South Brazil Current transports ~25 Sv of warm and saline SACW south in the western boundary current (Jullion et al., 2010) which is closely constrained against the continental slope. The Brazil Current forms the western limb of the South Atlantic Gyre. It is identified as more saline and with higher temperatures than the eastward moving SACW, with salinities up to ~36.7 psu. The Agulhas Current supplies subtropical Indian Ocean waters to the Atlantic via the Agulhas retroflection. The Agulhas Current is the western boundary current of the South Indian sub-tropical gyre driven by a large scale pattern of wind stress between the south east trade winds and the southern hemisphere westerlies (Lutjeharms, 2006). It flows along the east coast of Africa until separating from the continent where it loops anticlockwise feeding back into the Indian Ocean. Here it sheds rings and eddies into the Atlantic down to depths of 2000 m (Beal et al., 2006). This current is principally fed by these recirculating subtropical gyre waters, but is also fed by waters from the Red and Arabian Seas, the Indonesian through flow, and the equatorial Indian Ocean.

The Subantarctic Surface Water (SASW) forms from upwelled circumpolar deep water in the subantarctic and is transported north via Ekman transport. In their northward transport, surface nutrients are increasingly consumed by phytoplankton. The Antarctic Circumpolar Current (ACC) moves eastward through the Drake Passage, where part branches off to form the cold, fresh Malvinas Current (MC). The MC transports cold, fresh water of subantarctic origin and its transport has been estimated at ~30-33 ±7 Sv (Vivier and Provost, 1999; Spadone and Provost, 2009). The Brazil Current and Malvinas Current meet at the Brazil Malvinas Confluence (BMC), which is located at approximately 38°S (Garzoli and Garraffo, 1989). Within this region a large degree of cross frontal transport has been observed mixing subtropical and subantarctic waters, evidenced by complex thermohaline vertical and horizontal structures (Maamaatuaiahutapu et al., 1992). This large eddy field is believed to be the major region where water mass modification and exchange of heat and freshwater between the subtropical and subantarctic waters occurs (Gordon, 1989). The convergence of the two water mass types creates a very interesting region...
for marine biogeochemistry and allows the physical processes to be compared and their implications for marine productivity evaluated.

Figure 1.3 An overview of the main surface ocean currents in the South Atlantic basin. The 40°S transect lies across the South Subtropical Convergence, which moves north to south over the course of austral spring and summer. The location of the transect and the properties of the surface water masses captured are further defined in Chapter 3. Figure produced in Ocean Data View, current patterns based on Stramma and England, (1999).

1.3.2 Intermediate and deep water masses
The deep water masses of the Atlantic are identified in Figure 1.4. The Southern Ocean sourced waters have characteristic high nitrate and low salinity and are located at intermediate and bottom depths. The southward flowing North Atlantic Deep Water (NADW) intersects these waters with lower nitrate and higher salinity. The upper Meridional Overturning Circulation (MOC) comprises the Upper Circumpolar Deep Water (UCDW), Antarctic Intermediate Water (AAIW) and Subantarctic Mode Water (SAMW; Figure 1.4). The UCDW is composed of older water masses of the Pacific and Indian Oceans. The UCDW forms the base of the
intermediate waters entering the Atlantic Ocean, and contrasts from the AAIW and SAMW as it is not ventilated in the subantarctic. It is transported eastward in the ACC, formed by lateral mixing with subantarctic waters and further modified by the sinking organic matter (Sigman et al., 2000). Deep waters from ocean basins add to the UCDW on its eastward circumpolar circuit to form a mixture of Atlantic, Pacific and Indian deep waters (Oudot et al., 1999). The UCDW enters the Atlantic Ocean from the Drake Passage and moves northwards above the NADW and underlying the ventilated AAIW and SAMW at 40°S.

Circumpolar Deep Water upwells close to Antarctica and flows northward via Ekman Transport as Antarctic Surface Water (AASW). AASW is progressively freshened through air-sea fluxes and subducts at the Subantarctic Front (SAF) to form AAIW (Talley, 1996). A number of processes affect the formation of the AAIW such as convection within the mixed layer, Ekman transport, eddy fluxes and mixing within the SAF (Oudot et al., 1999). The SAMW is formed in the SE Pacific north of the Subantarctic Front (SAF) in winter as vertical mixing of the thermocline with the SASW (Piola and Georgi, 1982). These waters enter the Drake Passage and move northwards along the Western boundary of the South American coast via the Malvinas Current (Sloyan and Rintoul, 2001). At the Brazil-Malvinas Confluence (BMC), the SAMW is forced eastward and eventually northwards into the subtropical gyre in the Cape basin (Stramma and England, 1999). These waters circulate in the wind driven gyres and provide the mechanism by which Southern Ocean intermediate waters are ventilated and supply the subtropical regions with nutrients (Palter et al., 2010; Sarmiento et al., 2004).

The southward flow of NADW through the Atlantic ventilates the deep ocean, and these waters along with Antarctic Bottom Water (AABW) fill the global interior (Rahmstorf and England, 1997). The NADW is exported from the Atlantic and transported into the ACC, Indian and Pacific Oceans. It is formed from the surface waters of lower latitudes moving northwards, losing buoyancy and combining with sub polar waters. This process is driven by the northward transport of surface and intermediate waters from the south, and together with the AABW, these waters balance the southward flowing NADW. The AABW component is sourced from the
ocean bottom and extends northward through the North Atlantic into the Gulf Stream latitude. This water upwells into the southward flowing NADW above it. The AABW is the densest of oceanic water masses (Orsi et al., 1999). Its formation is concentrated on the Antarctic continental margins where mixing occurs between Circumpolar Deep Water (CDW) and shelf water. This occurs within the Weddell Sea, the Ross Sea and along the Adelie coast (Sloyan, 2006), with studies to date suggesting a dominance of Atlantic sources, in particular the Weddell Sea (Carmack, 1977; Orsi et al., 1999; Whitworth, 2002). Broadly, the circulation patterns in the South Atlantic are well characterised, although outstanding questions (e.g. inter-annual variability of southern source water fluxes, AAIW transfer at mid-latitudes, the role of Agulhas rings and leakage, and the influence of bottom topography) impact our understanding of processes driving MOC and the sensitivity of this overturning to change.

Figure 1.4 The deep water masses of the Atlantic Ocean, as identified by the nitrate concentrations and salinity. SAMW = Subantarctic Mode Water, AAIW = Antarctic Intermediate Water, UCDW = Upper Circumpolar Deep Water, AABW = Antarctic Bottom Water, NADW = North Atlantic Deep Water. The North Atlantic Deep Water has lower nitrate and higher salinity than the Southern Ocean sourced water masses. Figure produced in Ocean Data View using GEOSECs data.
1.3.3 Major N-cycling processes within the Atlantic basin

Nitrate supply to surface waters is essential for phytoplankton growth, it is therefore important to determine the sources of N which support primary production. The flow of nitrate within deep water masses also can provide indications of the global significance of different N-cycling processes, providing they can be characterised.

The South Atlantic is a region where both the deep and the surface waters can provide information about the sources and cycling of N on different timescales.

Nutrients are supplied to the surface of the open ocean in three main ways; upwelling or lateral transport of nitrate, N$_2$ fixation and atmospheric deposition. In all ocean basins nutrients are supplied to the low latitudes by the northward transport of the subantarctic water masses (Sarmiento et al., 2004). This return path of nutrients to
the low latitude ocean provides the necessary nutrients to sustain algae in the subtropical waters. This is the principal supply of $\text{NO}_3^-$ from the subsurface and as such the SAMW and the AAIW are particularly important to constrain due to the variability in their formation and certainties about changes in a warming climate. Without this process of resupply, it has been estimated that macronutrients in subtropical gyres would become depleted within 50 years (Palter et al., 2011).

Although the South Atlantic has long been thought to have low $\text{N}_2$ fixation rates, it remains understudied compared to the northern basin. Recent work suggests that the South Atlantic may be more important than previously thought (Moore et al., 2014). This is particularly due to the emerging knowledge of the importance of unicellular diazotrophs, which have been hard to detect through biological experiments. Newly fixed N that has not homogenised with the global ocean nitrate pool is likely to be retained and recycled in the surface subtropical water masses. Such retention/recycling has been observed, with suggestions of ~50% of nitrate in the subtropical gyres being sourced from $\text{N}_2$ fixation (Deutsch et al., 2001). Geochemical estimates using isotope studies may help to determine the relative importance of the two basins to basin wide $\text{N}_2$ fixation rates. Anthropogenic inputs of fixed N to the ocean are increasing, with an estimated global increase from 5.8 to 53.6 Tg N yr$^{-1}$ from 1860 to 2000, and, as such, the percentage of total fixed N that is anthropogenically-derived has increased from 29 to 80% (Duce et al., 2008). This is therefore likely to impact on N cycling processes. It is important to constrain the natural variability in these processes to identify the extent to which further change will affect productivity.

The inter-basin importance of the Atlantic in N-cycling processes can be explored via the inflow of waters from the South Atlantic and the exported NADW. The majority of the waters which form the NADW have been modified through their transport within the Atlantic basin. The NADW can therefore be studied to estimate the relative amount of nitrate which is sourced from internal cycling or new sources via $\text{N}_2$ fixation and atmospheric deposition. The sources of new N are important to constrain as they provide a means by which reactive N is added to the marine reservoir. Fixed N is principally lost from the global ocean via denitrification;
however denitrification rates are low in the Atlantic basin. Pelagic denitrification is not thought to be a major N sink in the South Atlantic and thus provides a unique difference to the Indian and Pacific Oceans. The main areas of denitrification are in shelf sediments and anoxic plumes with basin-wide rates of \( \sim 16 \text{ Tg N yr}^{-1} \). Atlantic shelf burial rates have been estimated at \( \sim 7.8 \text{ Tg N yr}^{-1} \) and a deep sea burial rate of \( 0.2 \text{ Tg N yr}^{-1} \) (Galloway et al., 2004). The extent of N loss is small compared to the net input of fixed N to the Atlantic, therefore the Atlantic may be a significant source of fixed N to the global ocean.

The Atlantic provides a unique region to study N cycling beyond stoichiometric studies. The deep waters formed in the North Atlantic fill half of the global deep ocean, formed from the inflow of intermediate waters which are exported through the South Atlantic. This basin also contrasts with the Indian and Pacific Oceans in that there are much lower denitrification rates, providing a unique investigation into basin-wide N-cycling processes. In previous N isotope studies the Pacific and Southern Oceans have been widely studied, yet there are sparse isotope signatures of subsurface nitrate from the Atlantic basin. This study increases this number extensively with the aim of investigating the role of the Atlantic basin in N cycling and to determine whether this role may be altered with climate-related changes in marine biogeochemistry.
1.4 The use of stable isotope tracers in marine biogeochemistry

Physical, chemical and biological processes can discriminate between the stable isotopes of a particular element. Fractionation of isotopes can occur through equilibrium or kinetic processes. The kinetic fractionation occurs in unidirectional reactions, whereby an element is converted from one form to another, e.g. C or N consumption by algae in surface waters. The isotope effect of a given reaction is defined by the rates at which the different isotopes are converted from reactant to product (reactions defined here using N):

\[ \varepsilon (\text{‰}) = \left( \frac{14}{15} k / \frac{15}{14} k - 1 \right) \times 1000, \quad (1.1) \]

where \( 14^k \) and \( 15^k \) are rate coefficients for \( ^{15}N \) and \( ^{14}N \).

Stable isotope studies utilise two idealised models of isotopic fractionation: the open system and the Rayleigh model. These models describe the isotopic composition of the reactant and product as defined by the isotope effect and the initial isotopic composition of the reactant. The Rayleigh model describes an environment where there is no resupply of the reactant and a constant isotope effect and can be defined with the following equations (defined here using N):

\[ \delta^{15}N_{\text{reactant}} = \delta^{15}N_{\text{initial}} - \varepsilon (\ln (f)) \quad (1.2) \]

\[ \delta^{15}N_{\text{instantaneous}} = \delta^{15}N_{\text{reactant}} - \varepsilon \quad (1.3) \]

\[ \delta^{15}N_{\text{integrated}} = \delta^{15}N_{\text{initial}} + \varepsilon \left( \frac{f}{1 - f} \right) \ln (f) \quad (1.4) \]

Where \( f \) = fraction of reactant remaining, and \( \delta^{15}N_{\text{initial}} \) = the initial nitrate isotope composition. When nutrients are resupplied to the surface via upwelling or the recycling and remineralisation of organic matter, samples tend to fall away from this trend, following open (steady state) system dynamics:

\[ \delta^{15}N_{\text{reactant}} = \delta^{15}N_{\text{initial}} + \varepsilon (1 - f) \quad (1.5) \]

\[ \delta^{15}N_{\text{product}} = \delta^{15}N_{\text{initial}} - \varepsilon (f) \quad (1.6) \]
The steady state system describes a system where the consumption is not reversible but is balanced by resupply with a constant isotope effect. Both Rayleigh and steady state fractionation is described in Figure 1.6.

![Figure 1.6 The isotopic fractionation of reactant and product N in a unidirectional reaction following open and closed systems. The graph demonstrates a fractionation factor (ε) of 5‰ demonstrating fractionation in the process of nitrate utilization by phytoplankton. The Rayleigh model applies when there is a closed pool of reactant N. The steady state applies when there is a continuous supply of reactant.](image)

The fractionation of stable isotopes in light elements provides spatially and temporally integrated tracers of biogeochemical processes. In this work stable isotopes are used in two ways. The principal use has been the measurement of the stable isotopes of $\text{NO}_3^-$. Nitrate has a relatively long residence time in the deep ocean but is more prone to consumption and recycling processes within the surface layer. This measurement can be used both in localized studies of the surface ocean but also as an integrative tracer in the deep ocean. In particular the development of the measurement of oxygen (O) isotopes within $\text{NO}_3^-$ has led to increased understanding of complex N-cycling processes. Biogeochemical processes are further assessed by measuring the isotopic ratios in organic matter. This is carried out through the
examination of suspended particulates and sediment core data to investigate the isotopic ratios in organic C and N. Together these measurements provide a comprehensive assessment of the C and N cycling in the South Atlantic.

1.4.1 Stable isotopes of nitrate (\(\delta^{15}N_{\text{NO}_3}\) and \(\delta^{18}O_{\text{NO}_3}\))

1.4.1.1 The use of geochemical tracers to understand the N cycle

Nitrogen cycling processes within the ocean are temporarily and spatially variable. Processes such as N\(_2\) fixation can be studied by determining rates of fixation in shipboard studies. However these snapshot measurements may provide an under or overestimation of this process over the course of seasonal variability. Due to these complexities, the development of integrative tracers is useful to avoid uncertainties in upscaling shipboard measurements of spatially and temporally variable N-cycling processes.

Nitrate and phosphate are well coupled within the ocean following a 16:1 stoichiometry from uptake and remineralisation by phytoplankton. Although the oceanic reservoir of phosphate is relatively constant, the nitrate reservoir is controlled by external inputs (N\(_2\) fixation) and outputs (denitrification). As such, the stoichiometry of N:P can be used to assess the importance of these two processes on regional, basin wide and global scales. The tracer N\(^*\) (calculated as NO\(_3^-\) – 16 x PO\(_4^{3-}\); Gruber and Sarmiento, 1997) calculates the concentration of nitrate excess or deficit within a sample compared to Redfield stoichiometry. Excess N (or an increase in N\(^*\)) can be produced by N\(_2\) fixation and a deficit (or decrease in N\(^*\)) can be produced from denitrification. Although an extremely important tracer for N cycling processes, there are some complications to its interpretation. Although on large scales nutrient remineralisation follows Redfield proportions (106:16:1), algal groups have varying nutrient requirements which can affect this. A high N:P stoichiometry may underestimate N\(_2\) fixation and a low N:P stoichiometry may overestimate N\(_2\) fixation. In addition, if N addition and loss are occurring in close proximity, the two processes may overlap, leading to their underestimation. N and O isotope signatures in NO\(_3^-\) (\(\delta^{15}N_{\text{NO}_3}\) and \(\delta^{18}O_{\text{NO}_3}\)) can be used as additional tracers of N-cycling processes, which help to overcome the difficulties of N\(^*\).
1.4.1.2 Nitrate sources and mean ocean reservoir

The average subsurface oceanic $\delta^{15}$N$_{NO3}$ is close to 5‰ and can be interpreted as a balance of new N to the ocean (principally $N_2$ fixation) and isotopic fractionation during denitrification (the principal loss of N from the ocean) (Galbraith et al., 2004, Figure 1.7). Nitrate added to the ocean by $N_2$ fixation is not fractionated during atmospheric $N_2$ uptake, therefore values of -2 to 0‰ are found in $\delta^{15}$N$_{NO3}$ or particulate nitrogen (PN) of $N_2$ fixation origin (Carpenter et al., 1997). This process adds NO$_3^-$ that is relatively depleted in $^{15}$N compared to mean subsurface NO$_3^-$. The mean subsurface nitrate is higher than this due to the effects of water column denitrification which consumes nitrate with an isotopic effect of ~25‰.

In most surface waters, NO$_3^-$ is fully consumed by phytoplankton. In these regions uptake and remineralisation is thought to have little effect on subsurface $\delta^{15}$N$_{NO3}$, as remineralised NO$_3^-$ should be similar to the source (Sigman et al., 2000). Therefore deviations in subsurface $\delta^{15}$N$_{NO3}$ can be indicative of processes far beyond the localized regions of water mass formation or NO$_3^-$ input/output. Thus on a local or regional scale, $\delta^{15}$N$_{NO3}$ will decrease with increased supply from $N_2$ fixation, and increase as NO$_3^-$ is lost via water column denitrification. The mean subsurface nitrate captures the isotopic fractionation from N loss compared to the light source $\delta^{15}$N from diazotrophs.
1.4.1.2 Nitrate consumption

The isotope effect of water column denitrification is 20-30‰ (Altabet et al., 1999; Brandes et al., 1998; Sigman et al., 2003) and the N loss during this process leaves an enriched imprint on $\delta^{15}N_{NO_3}$, which can be identified in water masses far beyond regions of denitrification (Sigman et al., 2005). Benthic denitrification, in contrast, leads to negligible fractionation of $\delta^{15}N_{NO_3}$ (Lehmann et al., 2004).
of water column and sedimentary denitrification can therefore be assessed from mean deep ocean $\delta^{15}$N$_{NO_3}$ (DeVries et al., 2012; Sigman et al., 2009, Figure 1.8).

Figure 1.8 Upper panel: Fractionation of $\delta^{15}$N nitrate and change in N* during N loss and N addition from the ocean. N addition decreases $\delta^{15}$N and increases N*. Water column denitrification increases $\delta^{15}$N and decreases N* and sedimentary denitrification does not affect $\delta^{15}$N nitrate but decreases N*. Lower panel: Fractionation of $\delta^{15}$N and change in N* with N loss. Sedimentary denitrification will affect N* but not $\delta^{15}$N, therefore this can be used to estimate the importance of sedimentary and water column denitrification within the ocean.
Nitrate consumption by phytoplankton also acts to enrich the residual pool of NO$_3^-$ in $^{15}$N, with an isotopic effect of $-5\%$ (Altabet and Francois, 2001). As noted above, in most regions of the ocean this enrichment does not impact subsurface NO$_3^-$ due to total assimilation. In the Southern Ocean, NO$_3^-$ concentrations remain high, a result of low light levels and iron limitation during photosynthesis (Boyd et al., 2001). Because of this, the process of NO$_3^-$ utilisation by phytoplankton can be investigated by determining the $\delta^{15}$N and $\delta^{18}$O compared to concentration, using Rayleigh fractionation (Sigman et al., 2000). Partial utilisation of nutrients leaves an isotopic imprint on preformed nutrients in intermediate waters from the Southern Ocean, of higher $^{15}$N and $^{18}$O with decreasing NO$_3^-$. The deviations away from the isotopic effect of NO$_3^-$ utilisation (5$\%$) can be used to indicate both physical and biogeochemical changes.

The O isotopes of NO$_3^-$ are consumed with the same isotopic effect as N ($^{15}\varepsilon=^{18}\varepsilon$) for both NO$_3^-$ utilisation and denitrification (Casciotti et al., 2002; Granger et al., 2004). Nitrate reduction is the dominant cause of fractionation for both of these processes (Needoba et al., 2004), which has been identified with similar fractionation for both isotopes ($^{15}\varepsilon/^{18}\varepsilon$) (Karsh et al., 2012). It has been found in numerous studies that as denitrification or NO$_3^-$ utilisation proceeds, the N and O isotopes become increasingly enriched along a 1:1 trajectory when plotted against NO$_3^-$ concentration (DiFiore et al., 2009; Sigman et al., 2009a; Rafter et al., 2013).

**1.4.1.3 Nitrate remineralisation**

In contrast to the consumption of NO$_3^-$, the production of NO$_3^-$ has different effects on $\delta^{15}$N$_{NO3}$ and $\delta^{18}$O$_{NO3}$. Fixed N added to the ocean via remineralisation of organic matter, is either sourced from non N$_2$ fixing phytoplankton, which have taken up in situ nutrients from the water column, or N$_2$ fixers which have a $\delta^{15}$N signature of $-1$. Non N fixing phytoplankton material will have a $\delta^{15}$N reflecting the uptaken N from the water column. In high nitrate environments this would be low as the lighter isotope will be preferentially consumed. In low nitrate environments (most regions of the ocean), the $\delta^{15}$N will be closer to $-5\%$, representing the integrated product. Close to ODZs remineralised nitrate $\delta^{15}$N may be higher due to water column denitrification. Therefore remineralisation of nitrate will have variable $\delta^{15}$N.
depending on the source of organic material, which may cover a large isotopic range (Figure 1.9).

**Figure 1.9** The isotopic range of remineralised nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$. The isotopic range of remineralised $\delta^{15}\text{N}_{\text{NO}_3}$ is variable in the ocean due to the recycling of fixed N within the ocean and the distinct isotopic source of newly fixed N. In contrast O atoms obtain their signature from the $\delta^{18}\text{O}$ of seawater plus an enrichment of ~1.1‰ from nitrification. The O isotope signature therefore is relatively constant in comparison to $\delta^{15}\text{N}$, which allows remineralisation processes to be studied from their coupled measurement.

In contrast to N atoms which are internally cycled within the ocean, O atoms in nitrate are obtained from ambient seawater and O$_2$. The newly nitrified $\delta^{18}\text{O}_{\text{NO}_3}$ therefore loses any previous enrichment from denitrification or partial utilisation processes and is an absolute input of O atoms to NO$_3^-$. In the process of nitrification $\delta^{18}\text{O}_{\text{NO}_3}$ is “reset”, with new NO$_3^-$ producing a signature of ~1.1‰ above the *in situ* $\delta^{18}\text{O}$ of seawater (Sigman et al., 2009). $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of seawater is relatively homogeneous, with typical values for the global ocean between -0.4 to 0.5‰ (Bigg and Rohling, 2000). Given the small range of variability in $\delta^{18}\text{O}$ of seawater, this process produces a relatively homogeneous isotopic signature (Figure 1.9, Casciotti et al., 2002; Buchwald et al., 2012). As nitrification is an absolute input of O, the
difference between δ\textsubscript{15}N\textsubscript{NO3} and δ\textsubscript{18}O\textsubscript{NO3} can provide information on the importance of nitrification vs. utilisation processes in the surface ocean. As δ\textsubscript{15}N\textsubscript{NO3} is dependent on the fixed N pool at the time of nitrification, it captures signatures that O isotopes do not. This allows their coupled measurement to assess the relative roles of processes such as NO\textsubscript{3}⁻ utilisation, which fractionates both isotopes equally, and addition of newly fixed N which affects δ\textsubscript{15}N\textsubscript{NO3} and δ\textsubscript{18}O\textsubscript{NO3} differently.

As a result, dual NO\textsubscript{3}⁻ stable isotope measurements can reveal the importance of assimilation and regeneration processes, and delineate and quantify the relative importance of different sources of fixed N (Sigman et al., 2005). Thus, δ\textsubscript{18}O\textsubscript{NO3} in combination with δ\textsubscript{15}N\textsubscript{NO3} is a powerful tool to constrain internal nitrate cycling further as the δ\textsubscript{18}O may record gross fluxes of NO\textsubscript{3}⁻. The difference in the processes that form NO\textsubscript{3}⁻ for N and O atoms has led to their dual measurement and the development of the parameter Δ(15-18) (defined here as δ\textsubscript{15}N\textsubscript{NO3} - δ\textsubscript{18}O\textsubscript{NO3}) (Rafter et al., 2013, Figure 1.10). This is increasingly used in NO\textsubscript{3}⁻ isotope studies to identify the different sources of remineralised NO\textsubscript{3}⁻ (Rafter et al., 2013). As both N and O isotopes are fractionated with the same isotopic effect for NO\textsubscript{3}⁻ consuming processes, a deviation away from a 1:1 relationship, and therefore shift in Δ(15-18), gives information about how NO\textsubscript{3}⁻ was formed. A low Δ(15-18) indicates the addition of low \textsuperscript{15}N (i.e. by remineralisation of newly fixed organic matter; δ\textsuperscript{15}N ~ -1‰, δ\textsuperscript{18}O ~1.1‰), and a high Δ(15-18) implies remineralisation in NO\textsubscript{3}⁻-deplete areas. This additional geochemical proxy for N-cycling processes has been used to estimate rates of N\textsubscript{2} fixation (Bourbonnais et al., 2009; Casciotti et al., 2008), denitrification and redox recycling (Sigman et al., 2005), and the regeneration of N from contrasting surface regions of the ocean (Rafter et al., 2013).
The dynamics of $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ fractionation in N cycling processes and the use of $\Delta(15-18)$. The isotope effect of nitrate consumption is similar for $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ resulting in 1:1 fractionation during these processes. In contrast, as O atoms are sourced from $\text{O}_2$ and $\text{H}_2\text{O}$ molecules with a relatively homogeneous value of $1 \pm 1\%$, deviations between $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ can be observed when remineralisation processes are occurring, either with the addition of light or heavy $\delta^{15}\text{N}$ compared to $\delta^{18}\text{O}$.

**1.4.2 Stable isotopes of organic matter ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$)**

The isotopic fractionation involved in C and N uptake can be used to assess phytoplankton variability, changes in uptake mechanisms and variable sources of reactant to the organism. In addition, the breakdown of organic matter affects C and N differently allowing the dual measurement to assess the remineralisation processes occurring in the water column.

Organic matter formation via photosynthesis involves considerable fractionation as the fixation of carbon preferentially utilises $^{12}\text{C}$, thus organic compounds are isotopically light compared to other carbon pools. A large fraction of carbon fractionation by phytoplankton is determined by $\text{CO}_2$ fixation by the enzyme...
Rubisco, which fractionates carbon by -31 to -22‰. However within the ocean the full fractionation is not normally expressed as many factors reduce the supply of CO$_2$ to the Rubisco enzyme. There are three steps in photosynthesis which strongly favour the uptake of $^{12}$C: (i) the uptake and intracellular diffusion of CO$_2$, (ii) the first CO$_2$-fixing carboxylation reaction, and (iii) translocation. Together they determine the extent of C isotope fractionation within phytoplankton. The biosphere can further be distinguished with C$_3$ and C$_4$ plants having different mechanisms of carbon fixation, allowing signatures of the different types to be identified (C$_3$ = -23 to -33‰, C$_4$ = -16 to -9‰). Nitrogen uptake follows a fractionation of 5‰ as previously described, apart from the utilisation of N$_2$ via diazotrophs which does not fractionate $\delta^{15}$N. These differences in C and N uptake allow the relative extent of terrestrial and diazotroph sources to be identified within the marine environment.

The breakdown of organic matter via respiration fractionates N isotopes, whereas there is little fractionation in the oxidation of C. This difference can be used to assess the degree of N fractionation occurring within the water column and the role of remineralisation processes. In contrast, the relative stability of $\delta^{13}$C allows its measurement in the deep ocean and sediments to retain a signature from its source. The relative sources and transport of marine and terrestrial organic matter in the surface and deep ocean can therefore be evaluated using isotopic signatures.
1.5 Thesis aims and research questions

The overall aims of this work are to increase the current understanding of the biogeochemical cycling of nitrogen and carbon in the South Atlantic through the use of N and C stable isotope signatures in the surface and deep ocean across a 40°S transect. Key areas of interest were highlighted at the start of the study with some specific research questions which are outlined in this section.

This dissertation also contributes to the international GEOTRACEs consortium increasing the global data set of $\delta^{15}$N$_{NO_3}$ and $\delta^{18}$O$_{NO_3}$ measurements.

1.5.1 Characterising nitrate isotope signatures in South Atlantic water masses

Initial research aims were to first investigate the N cycling processes which influence the biogeochemistry of South Atlantic water masses. This was investigated through the measurement of $\delta^{15}$N$_{NO_3}$ and $\delta^{18}$O$_{NO_3}$ across the South Atlantic 40°S transect. The causes of this variability can be used to assess the importance of different N cycling processes, integrated over the time scale of the water mass. The surface water masses are discussed in Chapter 3 and the deep water masses are discussed in Chapter 4.

1.5.2 Role of N$_2$ fixation in the Atlantic

The Atlantic is a region of the global ocean where denitrification does not occur at significant levels. If N$_2$ fixation is a significant process within this basin, there may be an imbalance between N loss and N addition and Atlantic N cycling may only be balanced on timescales of global ocean circulation. To assess this area of research, the role of N$_2$ fixation was investigated locally in the South Atlantic, on a basin-wide scale and also as a global comparison to the Indo-Pacific regions.

N$_2$ fixation in the subtropical South Atlantic (Chapter 3)

Nitrate isotope signatures in water masses can provide integrated signatures of N cycling processes in surface water masses. In this study, the role of N$_2$ fixation in supporting subtropical South Atlantic productivity was investigated. The principal aim was to assess the relative extent to which subsurface nitrate (NO$_3^-$), newly fixed N and atmospheric deposition provide fixed N to fuel primary productivity.
**Atlantic basin wide N₂ fixation (Chapter 4)**
A transect across 40°S provides a mechanism for studying waters imported into and exported out of the Atlantic basin. Because of this, one of the principal aims of this work was to investigate variability in nitrate isotope signatures in deep water masses to assess basin wide Atlantic N₂ fixation rates. The nutrient supply and stoichiometry of these water masses can be further investigated to investigate the controls on Atlantic N₂ fixation.

**Global N₂ fixation (Chapter 5)**
Atlantic data from this study can be compared to the current global dataset of nitrate isotope measurements to determine the importance of N₂ fixation and denitrification in each basin. This work was carried out to estimate the extent of global N₂ fixation compared to global denitrification rates to determine the relative balance between these two processes in the global ocean.

**1.5.3 Subantarctic vs. subtropical N cycling processes**
A transect across 40°S provides an opportunity to investigate the biogeochemical cycling of C and N in the south subtropical convergence where subantarctic and subtropical water masses meet. The frontal region is highly productive and provides a unique opportunity to determine the C and N cycling processes which dominate in the contrasting regions and across regions of mixing. The biogeochemical controls on primary production in these regions are investigated using N and C isotope data in Chapters 3, 5 and 6.

**1.5.4 The use of δ¹³C_{POC} as a palaeoproxy**
In a frontal region many processes may lead to C isotope fractionation in phytoplankton during uptake of inorganic C in the surface ocean. In many studies, the measurements of δ¹³C in sediments are used as a palaeoproxy for pCO₂. In this study, one research aim was to determine the applicability of δ¹³C_{POC} in determining pCO₂ in a zonal transect to assess the use of δ¹³C_{POC} as a palaeoproxy. This area of research is discussed in Chapter 6.
1.5.5 Fate and transfer of marine and terrestrial derived organic material

The South subtropical convergence is a highly productive region of the open ocean, where the convergence of contrasting nutrient regimes support large algal blooms. In this work, the role of marine productivity in C cycling processes is assessed to investigate the fate and transport of terrestrial and marine organic C in the South Atlantic. The relative importance of sources of C to the deep ocean from two contrasting continental margins and the surface open ocean are investigated in Chapter 6.
2 Fieldwork and Methods

This work was funded by the GEOTRACES programme, an international consortium which seeks to identify processes and quantify fluxes of trace elements and isotopes (TEIs) within the ocean, and to establish their sensitivity to environmental change. Many trace elements are critical for marine life and have direct implications for the marine C cycle and thus climate regulation. A diverse array of isotopes is used in modern biogeochemistry to assess ocean processes and to help understand the role of the ocean in past climate change. Despite this, there are a lot of uncertainties about the sources, sinks and internal cycling of TEIs in the ocean; mainly a result of the difficulties of sample collection and measurement techniques. The GEOTRACES programme aims to fill this gap with the quantification of processes which affect TEIs, through their measurement over a number of oceanic transects covering much of the global ocean.

The stable isotopes of nitrate ($\delta^{15}N_{\text{NO}_3}$ and $\delta^{18}O_{\text{NO}_3}$) have been identified as one of the key parameters to be measured on the GEOTRACES sections. Due to its importance as a proxy for present and past marine N cycling, these isotopes are to be measured on all GEOTRACES sections. In this study the focus has been on the use of the stable isotopes of nitrate, suspended particulates and sediment samples to characterise the biogeochemical cycling of N and C within the South Atlantic. The full suite of TEIs adds valuable information to explore N and C biogeochemical cycling further, through the use of fluxes and trace element cycling processes. The focus of the UK GEOTRACES consortium is the completion of these measurements across the 40°S transect of the South Atlantic (Figure 2.1). This region is highly productive and also an important junction between the North Atlantic and the Southern Ocean, which gives scope for a full analysis of the deep water masses of this region. The Natural Environment Research Council (NERC) funded the sample collection for this oceanic transect in austral spring for the undertaking of all TEI measurements. In measuring the stable isotopes of nitrate, this programme increases the number of measurements made within the Atlantic basin considerably, and adds to our understanding of the processes which fractionate this biologically important element within the global ocean.
2.1 Sample collection

The UKGEOTRACES transect started from Cape Town, sailing SW to the 40°S line, then due west across the South Atlantic section at this latitude. Samples were collected onboard the RRS Discovery between October and November 2010 (D357) and the RRS James Cook between December 2011 and February 2012 (JC068) as part of the UKGEOTRACES 40°S transect. The initial transect (D357) was not completed as the result of a medical evacuation, but a complete set of samples from the Cape basin were collected (Figure 2.1). The remaining ship time was also used to increase the resolution of sampling from the Cape basin. The JC068 cruise completed the transect across both the Cape and Argentine basins, extra surface sampling of all stations and intercalibration of Stations 3 and 6 (Figure 2.2).

![Figure 2.1 Map of study region, with sampling stations numbered. Samples were collected in an east to west transect. Colours denote sea surface temperature (°C). Figure adapted from Browning et al. (2014).](image)

Standard CTD (conductivity, temperature, depth) measurements and water sampling were performed using a 24 position stainless steel rosette equipped with a full sensor array and 24 20-litre OTE bottles. Nitrate, nitrite, phosphate and silicate concentrations were determined using an AA III segmented-flow Auto Analyser (Bran & Luebbe) following colorimetric procedures (Woodward and Rees, 2001). Ammonium concentrations were analysed using the gas diffusion of ammonia across a Teflon membrane from a differential pH gradient. Ammonia reacts with a
fluorescent reagent and is subsequently detected by a Jasco fluorometer. Salinity, temperature and depth were measured using a CTD system (Seabird 911+) and salinity was calibrated on-board with discrete samples using an Autosal 8400B salinometer (Guildline). Dissolved O$_2$ was determined by a Seabird SBE 43 O$_2$ sensor and calibrated using a photometric automated Winkler titration system (Carritt and Carpenter, 1966). Water samples for nitrate isotope analysis were collected from the stainless steel rosette. Seawater was filtered through an Acropak filter (0.45 µm) into HCl clean 60 ml Nalgene bottles and frozen at -20 °C and transported back to the UK onboard the vessel, frozen. Two bottles were filled at each depth, covering the whole water column at each station.

Figure 2.2 Sample collections on both cruise legs. Intercalibration of deep samples from stations 3 and 6 are identified, colours represent NO$_3^-$ concentrations (High=Red, Low = purple). The surface 400 m was sampled at each station on JC068 to account for inter-cruise variability in surface water masses.
For the collection of suspended particulate samples, GF/F microfibre filters (0.7 µm pore size, 25 mm diameter) were used. Prior to embarking on each cruise, filters were muffle-furnaced at 450 °C for four hours. Filters were individually weighed on a microbalance, wrapped in aluminium (Al) foil and sealed in a plastic container for transportation. Water was primarily collected in the surface 400 m; when the water budget allowed, deeper samples were also taken from the regular rosette. Two to four litres were taken from the high chlorophyll surface waters and 8-20 litres from deeper waters. Approximately eight sample depths were collected from each station and collected into 10 litre carboys. Each water sample was pressure filtered simultaneously using a compressor (at ~10 psi) and an 8-way manifold system (Figure 2.3), and filtered within two hours of collection. Once the total volume for each depth was filtered, Milli-Q water was run through the filters to remove salts, and then filters were extracted from the filter holder, placed in labelled aluminium foil and dried at 50 °C for ~12 hours. Once dried, filters were folded, placed in ziplock bags and frozen at -20 °C. Carboys and tubing were rinsed with 10% HCl and then further rinsed three times with Milli-Q water between sample collections. GF/F filter holders were rinsed, put in 10% HCl acid bath overnight and rinsed with Milli-Q.

Sediments were collected using a box mega corer; samples were removed from the coring frame and immediately transferred to the Constant Temperature (CT) laboratory on board set close to bottom water temperatures. Sediment cores were sliced in 2 cm slices; a sub sample of ~1 cm³ was taken from each slice, stored in a ziplock bag and frozen at -20 °C for δ¹³C and δ¹⁵N analysis in the laboratory at the University of Edinburgh. Stand Alone Pump systems (SAPS) were deployed at super stations in two separate deployments (shallow and deep), generally pumping for 2 hours and filtering hundreds to thousands of litres. The SAPS collected particles using 2 stacked 293 mm diameter pre combusted GF/F filters (0.7 µm nominal pore size). GF/F filters were recovered in a fume hood, wrapped in ashed Al foil and frozen at -80 °C. A section of each GF/F filter was collected frozen, and taken back to the University of Edinburgh for δ¹³C and δ¹⁵N analysis.
2.1.1 Intercalibration between cruises

Intercalibration between the two cruises was carried out to ensure that the deep samples were similar in their concentrations and isotopic ratios. To account for changes in the biology in the surface layer, the surface rosette was sampled at each station for both of the cruises. The deep samples were hypothesised to be similar and are compared in Figure 2.4. Here it is shown that the isotopic measurements of nitrate are similar over both cruises at depths greater than 500 m. Variability in the surface 500 m is observed in Station 3, with the movement of the Agulhas retroflection. In D357, the core of the Agulhas ring was identified at Station 2 whereas in JC068, this was identified in Station 3. This is observed in the isotopes as well as salinity, temperature and nutrients. In D357, enrichment in $\delta^{15}N_{NO_3}$ is observed into the surface waters, whereas in JC068, with the influence of the subtropical Agulhas Current, the $\delta^{15}N_{NO_3}$ is increasingly lighter to the surface. This
observed trend towards lighter values correlates with increasing salinities and temperatures and decreasing nitrate concentrations.

Figure 2.4 Intercalibration between D357 and JC068. A large deviation in the isotopic signatures in the surface 500 m of Station 3 is a result of variability in the Agulhas current between D357 and JC068. In D357, the Agulhas core was identified in Station 2 and in JC068 it was identified in Station 3. The lower $^{15}$N in JC068 correlated with higher salinities, temperatures and lower nitrate concentrations typical of the Agulhas leakage.
2.2 Isotopic measurements

The isotopic composition of NO$_3^-$, particulate organic matter (suspended) and sediment organic matter was determined to examine the biogeochemical cycling focussed at 40 °S. Mass spectrometry can measure the precise ratio of different isotopes within a sample to determine the natural deviations away from reference material with a constant ratio. Isotopic ratios are typically presented in their delta notations (δ) which are calculated using Equation 2.1. Each element is analysed relative to a universal reference (carbon = Peedee Belemnite (PDB), nitrogen = Air (AIR) and oxygen = Vienna Standard Mean Ocean Water (VSMOW)).

$$\delta_{\text{sample}} = \frac{R_{\text{sam}}}{R_{\text{std}}} - 1$$  \hspace{1cm} (2.1)

$R_{\text{sam}}$ and $R_{\text{std}}$ are the stable isotope ratios for the sample and standard. For C, N and O, these isotopic ratios are $^{13}/^{12}$C, $^{15}/^{14}$N and $^{18}/^{16}$O and are reported in per mil (‰).

Mass spectrometry separates charged atoms and molecules by their mass using electric and magnetic fields. Positive ions produced by bombarding gas molecules with electrons from a heated filament, are then accelerated and focussed. From a source, ions enter the magnetic field sector where they follow circular field trajectories, and their radius is determined by the mass to charge ratio (m/z). At the end of the magnetic sectors, Faraday cups collect the different ion beams. Samples to be measured by isotope ratio mass spectrometry (IRMS) are converted to a clean gas which can be introduced to the gas source of the mass spectrometer. There are two types of inlet system, dual inlet and continuous flow. Dual inlet systems allow the consecutive analysis of a sample and reference gas pair using a changeover valve. In continuous flow inlet systems, samples and reference gases are added to the mass spectrometer by the use of a He carrier gas and a gas preparation system is typically used to separate sample compounds using a gas chromatograph. In the methods used here, continuous flow mass spectrometry (CF-IRMS) is used, with specific techniques adopted to isolate the sample gas (N$_2$O, N$_2$, CO$_2$) from other gases present within the sample. These techniques are outlined below.
2.2.1 Denitrifier Method (isotopic analysis of nitrate)

Nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ were measured via the bacterial conversion of nitrate to nitrous oxide via the Denitrifier Method (Casciotti et al., 2002; Sigman et al., 2001). Samples analysed in the first three years of this study were undertaken at the Scottish Universities Environmental Research Centre (SUERC). This was done via isotopic analysis of nitrous oxide using a custom built Gas Chromatography-IRMS (GC-IRMS) system in line with a VG Prism III isotope ratio mass spectrometer at SUERC. Further samples were analysed at the University of Edinburgh using a Gas Bench II coupled with a Delta Advantage + MS.

The bacterial conversion of nitrate to nitrous oxide by denitrifying bacteria, has been used in a wide number of marine studies to measure the natural abundance of nitrogen and oxygen isotope ratios in nitrate (e.g. Hastings et al., 2004; Lehmann et al., 2005; DiFiore et al., 2006; Ren et al., 2009). This method was initially developed using the bacterial strain Pseudomonas chlororaphis (Sigman et al., 2001), which lack the nitrite reductase enzyme to convert nitrous oxide to N$_2$ gas. The technique was further developed to use Pseudomonas aureofaciens which uses copper-type nitrite reductase (Glockner et al., 1993) reducing the exchange of oxygen atoms in water with N$_2$O (~6 %) (Ye et al., 1991) and allowing for the determination of the oxygen isotopes of nitrate (Casciotti et al., 2002). The method has dramatically decreased sample size requirements and analysis time compared to previous methods (Johnston et al., 1999; Revesz et al., 1997; Sigman et al., 1997). Over the course of this study, the Denitrifier Method has been developed initially at the SUERC and further at the University of Edinburgh. Additional development of the initial method (Sigman et al., 2001, Casciotti et al., 2002) has taken place since these publications. Many of these improvements are mentioned in McIlvin and Casciotti (2011), and will be outlined below.

Initial work on this method at SUERC between 2006 and 2008 proved to be unsuccessful in developing a reliable isotopic analysis of nitrate. It was speculated that analytical problems may have resulted from the strain of bacteria used (P.chlororaphis), which may have differed significantly from strains used in other
laboratories adopting this method. Other possible problems were associated with the cryogenic focusing system and the gas preparation system. Further work was carried out by Sian Henley (University of Edinburgh) from 2009 – 2011 into the development of the method using *Pseudomonas aureofaciens*. From initial visits to the University of East Anglia (Sian Henley, Robyn Tuerena) and Woods Hole Oceanographic Institution (Sian Henley) in 2009-2010, the method was successfully set up for the analysis of δ15N of nitrate at the Scottish Universities Environmental Research Centre. Over 2009-2011 (Sian Henley 2009-2011, Robyn Tuerena 2010-2011), the method was modified and improved to solve initial issues and to improve the accuracy of N isotopic values produced. A number of changes to both the microbiology techniques for bacterial conversion of NO3− to N2O and the isotopic analysis of N2O were made. The changes that took place to the method are based on the methods used by Princeton University, Woods Hole Oceanographic Institution and University of East Anglia. After the initial success of method development at SUERC, the method was further developed at the University of Edinburgh for measurement of both δ15N and δ18O of nitrate (Robyn Tuerena 2012-2014, for more details on method development, see Appendix 1).

The success of the method development was determined through quality control measures which were continued throughout sample analysis. To test reproducibility, all samples were run in duplicate in each run, and further samples (>3 per run) were analysed in a separate run to check inter-run variability. Blanks and standards are used in each analysis, the standard deviation of standards was tested to ensure a reliable run and to ensure no problems with bacteria batches. If blank values were detected, the run was not used any further.

### 2.2.2 Bacterial conversion of nitrate to nitrous oxide

This method involves the culturing of denitrifying bacteria, to be used to convert sample NO3− into N2O, and requires clean laboratory conditions for microbiology. A bacterial strain of *Pseudomonas aureofaciens* was obtained as frozen stock (Karen Casciotti, Woods Hole Oceanographic Institution, 2010) and stored frozen at -80°C. This strain was used to allow for the isotopic analysis of δ18O in addition to δ15N.
Bacteria is revived from frozen stock and cultivated on tryptic soy agar plates for 3-4 days, before re-streaking with an individual colony onto a new plate. The growth of bacteria is monitored and any contaminated plates are discarded. To minimise any contamination all work is done under a laminar flow hood, the surfaces are cleaned with 70% ethanol and gloves are worn at all times. The inoculating loop is sterilised by flame until it glows red, and this is repeated between each streak. Starter tubes containing 7 ml of media are inoculated with an individual colony of bacteria and grown overnight on an orbital shaker. Larger 160 ml cultures are inoculated from the starter tube by the addition of 0.7 ml of media using a syringe to inject crimp seal media bottles. These cultures are left to grow on the orbital shaker for 6-8 days to ensure sufficient growth of bacteria.

Following the incubation period, the media is divided into 50 ml aliquots to be centrifuged at 5000 g for 30 min. The supernatant media is poured off and 100 ml of nitrate free media (NFM) is added to re-suspend bacteria in a 3-4x concentration of bacterial cells (Sigman et al., 2001). The bacterial media is pipetted in 3 ml aliquots into 20 ml glass vials and crimp sealed using butyl septa. Butyl septa were used in replacement of silicone septa as they have higher gas impermeability and efficiently prevent leakage from vials for >165 days (McIlvin and Casciotti, 2011). To remove any N₂O and ensure anaerobic conditions prior to sample injection, vials are purged with N₂ gas for over three hours. Purging was carried out using a custom built purge rack where 23 G syringe needles are mounted into rubber bungs. 19 G syringe needles are inserted into the butyl septum of each vial and samples are then inverted and placed onto the purge rack. To take samples off the rack, the 19 G needle is removed and the vial is quickly removed from the rack to prevent any pressure build up within the vial. Once the vials have been purged for more than three hours, a known concentration of nitrate from the seawater sample or standard is added to each vial. 60 nmol of NO₃⁻ (30 nmol N₂O) was initially used, but was changed to 30 nmol, with further development of the technique at the University of Edinburgh. Using the same concentrations through sample runs avoids any linearity problems in the isotopic determination by IRMS. Isotopic standards used within our laboratory are N₃, USGS-32, USGS-34, and USGS-35, in which 0.15 ml of 200 µmol standard
solution is added to each vial for a 30 nmol concentration. The sample vials are left in the dark at room temperature overnight, to allow complete conversion of NO$_3^-$ to N$_2$O. The following day the bacteria are lysed by adding 0.1-0.2 ml of 10 N NaOH to each sample vial, which also immobilises CO$_2$ within the vial. The samples are then ready for analysis by IRMS.

As a higher concentration of nitrate was used for isotopic analysis at SUERC (60 nmol), a larger volume of seawater was required to analyse low concentration samples (less than 2 µM NO$_3^-$). To do this, 160 ml crimp seal bottles were used in place of 20 ml sample vials. Since the volume of sample injected into each vial should not exceed 5x the volume of cell concentrate; 6 ml of cell concentrate was used with this adaptation of the method. To ensure all contamination within the vials is removed prior to sample injection, the purge time was increased to 5 h for the increased sample size. The required purge time was tested over a number of prior runs, to ensure all reactive N was removed from the bottle prior to sample injection. Adoptions were also made to the gas prep system with an increased freeze time of 15 minutes to ensure the maximum amount of sample is focussed for isotopic analysis. This method provided accurate measurements of δ$^{15}$N to 1σ=0.2‰, for samples with concentrations as low as 2 µmol L$^{-1}$.

### 2.2.3 Isotopic analysis of nitrous oxide

#### 2.2.3.1 Scottish Universities Environmental Research Centre (SUERC)

The Denitrifier Method (Sigman et al., 2001; Casciotti et al., 2002) has been used in combination with a VG Prism III isotope ratio mass spectrometer at SUERC. The analytical set up includes a custom built GC-IRMS system with an Analytical Precision gas prep interface and a cryogenic focussing system to separate the N$_2$O. Following the initial problems identified from previous work on this method at SUERC, the system was modified to the set up identified in Figure 2.5.

Sample N$_2$O within the headspace of each vial is flushed using He as a carrier gas through an ethanol slush trap at -60 °C to remove water and volatile organics. The sample then passes through a magnesium perchlorate/carbosorb trap to further remove water and CO$_2$. The sample passes into a liquid nitrogen trap, and is
cryogenically focussed for 6 minutes. The valco valve is switched to inject mode and N$_2$O and any remaining CO$_2$ or water passes into a GC column, where they are separated into different pulses by gas chromatography, before reaching the open split of the IRMS. Continuous flow isotope ratio mass spectrometry measures the m/z ratio of each sample and standard versus the reference N$_2$O. Molecular N$_2$O ion measurements at 44, 45 and 46 are provisionally referenced to N$_2$ and VSMOW, by normalizing to the N$_2$O reference peak. For the absolute reference of NO$_3^-$ isotopes, the standards that are run simultaneously to the samples are used. As the amount of standard NO$_3^-$ is matched to that of the samples, this corrects for the non-linearity of the mass spectrometer and the blanks associated with the analysis. The slope and intercept of the linear regression between the measured standards and the known isotopic ratios within the standards is then used to correct the samples to their absolute isotopic values (Table 2.1). All sample runs from SUERC that are used within this study had blank sizes below the detection limit of the mass spectrometer. However the effects of blanks are likely to be similar across the whole batch and therefore are corrected for in standard corrections. Using this methodology and instrumentation, sample reproducibility for $\delta^{15}$N was found to be 1σ=0.2. The $\delta^{18}$O data were found to be much more variable which is presumed to be an effect of the gas prep system. For this reason, and the need for precision when measuring deep water samples, the $\delta^{18}$O was not used from numbers produced from SUERC, but were used instead by the more recent set up from the University of Edinburgh (See below).

Table 2.1 Reference standards used for nitrate isotopic analysis. Isotopic values are stated relative to AIR and VSMOW, respectively.

<table>
<thead>
<tr>
<th></th>
<th>$\delta^{15}$N$_{NO3}$ (‰ vs. AIR)</th>
<th>$\delta^{18}$O$_{NO3}$ (‰ vs. VSMOW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAEA-N3</td>
<td>+4.7</td>
<td>+25.6</td>
</tr>
<tr>
<td>USGS-32</td>
<td>+180</td>
<td>+25.7</td>
</tr>
<tr>
<td>USGS-34</td>
<td>-1.8</td>
<td>-27.9</td>
</tr>
<tr>
<td>USGS-35</td>
<td>+2.7</td>
<td>+57.5</td>
</tr>
</tbody>
</table>
Figure 2.5 Initial set up of the GC-IRMS system at SUERC. Sample load indicates the set-up in which the sample is added to liquid N$_2$ trap. Inject mode shows how He carries the sample through the GC system and to IRMS. Lines shown in bold indicate the pathway of the sample in each of these modes. For details of sample run see information in text.
2.2.3.2 University of Edinburgh

The method used for bacterial conversion of nitrate to nitrous oxide at SUERC was used at the University of Edinburgh. The only changes made to this were to increase the throughput of samples, by the construction of a purge rack for the use of 40 samples. The analysis of 40 samples per day was possible with the new set-up of the method, in particular the IRMS set up. The higher sensitivity of the instrument allowed for lower concentrations of nitrate to be used for analysis and thus 30 nmol concentration samples were prepared, requiring a lower volume of sample per analysis. Samples were analysed using a Gas Bench II with denitrification set up and coupled to a Delta Advantage + MS. A purge and trap system was set up in line with the Gas Bench II, and initial testing of the system was carried out using isotopic standards (USGS 32, USGS 34, USGS 35, see Table 2.1).

The full purge and trap system is outlined in Figure 2.6. The sample is purged from the vial with He carrier gas at 20 ml min\(^{-1}\) and passed through a permapure trap, an ascarite and a nafion trap to remove water and CO\(_2\). Sample N\(_2\)O is then trapped in the first liquid N\(_2\) trap and as the system is switched to inject mode, He carries the sample into a second liquid N\(_2\) trap at 2 ml min\(^{-1}\). Once this trap is lifted from the system, it passes through the GC column to separate N\(_2\)O from any remaining CO\(_2\) and H\(_2\)O present. From the GC column, the sample passes through a second nafion trap which then passes into the sample open split and into the mass spectrometer. Prior to the sample, the reference gas is injected into the reference open split. The sample peak is analysed in comparison to the reference peak and then standardised to the isotopic ratios of the standards after the analysis run. The analysis of samples using the Gas Bench II improved the precision of isotopic measurements, especially for \(\delta^{18}\)O measurements. This set up also allowed for higher sensitivity and lower volumes of sample could be used for each analysis. The improvements were thought to be a result of a more efficient purge and trap system which is closer in line with modifications to the system as described by McIlvin and Casciotti (2011).
Figure 2.7 The Gas Bench set up at the University of Edinburgh. Sample load indicates the set-up in which the sample is added to liquid N\textsubscript{2} trap 1. Inject mode shows how He carries the sample through the GC system and to IRMS. Lines shown in bold indicate the pathway of the sample in each of these modes. For details of sample run see information in text.
2.2.4 Intercalibration between SUERC and University of Edinburgh

The initial samples analysed for this study were measured at SUERC. To ensure that the data between the two mass spectrometer set ups were comparable, an intercalibration was made. A paired t-test was carried out for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ from SUERC and the University of Edinburgh. For both tests there was no significant difference between the two analyses ($\delta^{15}\text{N} p=0.39$, $n=20$, $\delta^{18}\text{O} p=0.79$, $n=18$). Higher precision and reproducibility was found with the system at the University of Edinburgh and allowed $\delta^{18}\text{O}$ measurements to be used to a higher degree of certainty.

![Intercalibration between samples from SUERC and University of Edinburgh. Samples run at SUERC are shown with closed circles and samples run at the University of Edinburgh are shown with open triangles. Higher precision is evident in the samples run at the University of Edinburgh with the smaller error bars.](image)
2.2.5 Caveats and Future directions
The development of the Denitrifier Method at both SUERC and University of Edinburgh now provides precision of measurements of both δ¹⁵N and δ¹⁸O of nitrate to 0.2 standard deviation, and to nitrate concentrations as low as 0.5 µmol L⁻¹. This is comparable to many laboratories around the world which adopt this method. The successful development of the Denitrifier Method for the isotopic analysis of seawater nitrate has many applications, and the method can be further developed in future work to cover a wide number of isotopic applications. Using the bacterial conversion of nitrate to nitrous oxide, this method can also be applied to:

- Groundwater
- Stream water
- Sea and glacial ice
- Soil extracts
- Dissolved organic nitrogen (DON)

The method has also been applied to Palaeoceanography studies, with the isotopic analysis of organic N bound within diatoms and foraminifera. These developments can reduce the error in palaeo measurements from diagenesis processes within sediments. A number of these methods and applications may be developed further for the continued use of this method in N isotopic studies.

2.3 Organic matter in suspended particulates and sediment samples
2.3.1 Suspended particulates

To determine the isotopic composition of particulate organic carbon (δ¹³C_{POC}) and particulate organic nitrogen (δ¹⁵N_{PN}) in suspended particulates, the material collected on GF/F filters are analysed. Before preparation for analysis, samples are weighed to calculate the suspended particulate matter (SPM) on each filter. Prior to analysis, carbonates were removed by acidification with concentrated HCl. GF/F filters are wetted with Milli-Q water and placed in a desiccator with 70% v/v HCl for 48 hours. To ensure all the carbonates are removed, a drop of acid is pipetted onto one filter. If any effervescence occurs the filters are left for a further 24 hours. Once all the
carbonates have been removed, the filters are dried for 12 hours at 50 °C and folded into tin cups ready for analysis.

2.3.2 Sediments
Sediment samples were initially freeze dried, and then homogenized by grinding with a pestle and mortar. From initial estimates of organic content, a certain weight of each sample was measured into silver capsules, which are held in a sample rack. The capsules were acidified under a clean laminar flow bench by pipetting drops of 50% HCl into the capsules, carefully to avoid over effervescence and loss of sample. Samples were heated to 50 °C and HCl added every few hours until all carbonate was removed. Silver capsules were then folded ready for analysis.

2.3.3 Elemental Analysis (EA) and IRMS
For the measurement of δ\(^{13}\)C and δ\(^{15}\)N of organic matter, samples were analysed using a Carlo Erba NA 2500 elemental analyser in-line with a VG PRISM III isotope ratio mass spectrometer for elemental POC/PN and δ\(^{13}\)C\(_{POC}\) and δ\(^{15}\)N\(_{PN}\). Samples are dropped into a combustion column, where C and N are combusted to CO\(_2\) and N\(_2\), passed through a reduction column, where excess O\(_2\) is removed and nitrogen oxides are converted to N\(_2\) gas. Following this, gases are passed through a GC column introducing a delay between nitrogen gas and CO\(_2\). The output of the IRMS presents raw ratios of the standards and samples. Any drift is identified using internal standards which are run approximately every 10 samples throughout the batch. The final delta values are corrected using internal standards.

Weighed internal laboratory standards of PACS and acetonilide were also folded into identical tin/silver capsules. PACS samples were used for the isotope corrections and acetonilide was used for investigating the elemental composition of the sample. The concentrations of POC and PN for filters were then calculated using SPM and the \%wt.C and \%wt.N of measured material.

2.4 Data analysed as part of thesis
In this work, I collected, analysed and interpreted all isotopic measurements of δ\(^{15}\)N\(_{NO3}\), δ\(^{18}\)O\(_{NO3}\), δ\(^{13}\)C\(_{POC}\), δ\(^{15}\)N\(_{PN}\) from 40°S that are in this thesis. I also analysed
further samples of $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ from the Arctic Ocean and Southern Ocean as outlined in Chapter 5. In addition I produced all measurements of particulate organic carbon and nitrogen used within this thesis.

2.5 Ancillary data

Additional data has been used within this thesis for complimentary use with stable isotope data. These data have been analysed by a number of scientists from the GEOTRACES community and are acknowledged for their help throughout this work:

Nutrient data (nitrate, nitrite, phosphate, silicate and ammonium): Malcolm Woodward (Plymouth Marine Laboratory)

Oxygen data: Sue Reynolds (University of Tasmania) and Cynthia Dumoussoud (University of Southampton)

Particle fluxes, derived from $^{234}\text{Th}$ dating: Katsia Pabortsava and Patrick Martin (University of Southampton)

Biological data: Tom Browning and Heather Boumann (University of Oxford)

Carbonate system: Matthew Humphries and Cynthia Dumoussoud (University of Southampton)

$\delta^{13}\text{C}$ of dissolved inorganic carbon: Alex Piotrowski and Jo Clegg (University of Cambridge)

Particulate Al: Angela Milne and Maeve Lohan (University of Plymouth)

2.6 Production of cross section plots

All cross section plots used in this work are produced using ODV and DIVA gridding software which was developed at the University of Liege (http://modb.oce.ulg.ac.be/projects/1/diva). DIVA allows analysing and interpolating data in an optimal way, comparable to optimal interpolation (OI). Unlike OI, DIVA also takes into account coastlines and bathymetry features to structure and subdivide the domain on which estimation is performed. Calculations are performed on a finite element mesh adapted to the specific gridding domains.
3 Identifying sources of fixed N to the south subtropical convergence

3.1 Abstract

The South subtropical convergence is a region of high productivity, here nitrogen and iron limited waters meet, supplying the necessary nutrients to sustain high levels of algal biomass. The stable isotopes of nitrate ($\delta^{15}$N$_{NO_3}$ and $\delta^{18}$O$_{NO_3}$) are used to assess the cycling of fixed N in this region and its influence on productivity. The supply of fixed N to the mixed layer is documented across the subtropical front using dual isotope signatures. An isotope effect of 5‰ is observed from the process of algal consumption, suggesting a similar fractionation of nitrate by phytoplankton throughout the Southern Ocean. Low $\delta^{15}$N$_{NO_3}$ relative to $\delta^{18}$O$_{NO_3}$ is identified in both the subtropical and subantarctic water masses, although contrasting N cycling processes are identified. South of the front, the lateral supply of macronutrients from the subantarctic fuels primary production. Iron limitation, results in a low biological demand for N and residual NH$_4^+$ is identified in the upper water column. Incomplete ammonium oxidation leads to lower $\delta^{15}$N$_{NO_3}$ in relation to nitrate concentrations. Low $\delta^{15}$N$_{NO_3}$ and $\Delta$(15-18) resulting from incomplete ammonium oxidation are likely be common in the subantarctic and should be taken into account in future studies of nutrient dynamics in this region. In the subtropical water masses, recycling processes dominate supply of nutrients to surface waters. Here the relative supply of nutrients has been assessed using the isotopic signatures in nitrate and particulate N combined with $^{234}$Th fluxes. Newly fixed N supports 30-50% of production in the South Atlantic Central water and Agulhas Current. This finding highlights the importance of diazotroph abundance to primary production in subtropical gyres where fixed N limits production. Fixed N supplied from N$_2$ fixation accounts for ~ 75% of the production at the core of the Brazil Current. This high estimate indicates that diazotrophs may be present in the SW Atlantic and supply a significant source of new N to the Atlantic basin.
3.2 Introduction

Nitrogen is the principal limiting nutrient in the low latitude ocean, where concentrations of fixed N (ammonium, nitrate, nitrite) are low and limit the growth of phytoplankton (Tyrrell, 1999). These subtropical regions constitute a large proportion of the global ocean, and the supply of fixed N to the surface ocean has large implications for marine productivity. Nitrate (NO$_3^-$) is added to the surface mixed layer by physical exchange with high nutrient waters, conversion of N$_2$ into organic matter by N$_2$ fixation and atmospheric deposition (Baker et al., 2003; Sarmiento et al., 2004; Mahaffey et al., 2005). As these processes are temporally and spatially variable, it is difficult to quantify their relative importance. The South Atlantic remains one region of the global ocean where the importance of these N cycling processes remains relatively understudied. At ~40°S, the south subtropical gyre and the subantarctic surface waters converge to create a highly productive region of open ocean. In this study, the different processes which supply fixed N to the surface of this region are assessed and their implications for productivity are discussed.

The addition of new N via N$_2$ fixation and atmospheric deposition are the principal sources of new N to the Atlantic subtropical basin. Yet the importance of new N in supplying productivity in the South Atlantic is poorly understood. The subtropical North Atlantic has long been identified as a region where N$_2$ fixation is likely to play a dominant role in primary productivity (Mahaffey et al., 2005). This is seen to be fuelled by the supply of dust from the Sahara (Mills et al., 2004) and the supply of phosphorous (PO$_4^{3-}$) from intermediate water transport (Moore et al., 2009). Although the role of N$_2$ fixers in the North Atlantic has been studied for decades (Hansell et al., 2007; Michaels et al., 1996), their importance in the subtropical South Atlantic has received less attention. Diazotrophs, in particular the species *Trichodesmium*, have been found to be abundant between 0-15°N, but almost completely absent between 5-30°S (Tyrrell et al., 2003), leading to much lower estimates of N$_2$ fixation in the South Atlantic (Moore et al., 2009). The abundance of N$_2$ fixers has been identified as low in studies of the subtropical South Atlantic (Tyrrell et al., 2003; Sohm et al., 2011). A recent study however has highlighted the
possibility of a dominance of unicellular diazotrophs in the South West Atlantic, highlighting that the role of diazotrophs in the South Atlantic remains unclear (Moore et al., 2014). Even if diazotrophs have a low abundance in the South Atlantic, recently fixed N from the North Atlantic may still provide an important source of newly fixed N. Here I aim to assess whether newly fixed N contributes to productivity in the south of the South Atlantic gyre.

The South Atlantic plays a vital role in communicating between the relatively nutrient-poor North Atlantic and high nutrient low chlorophyll (HNLC) Southern Ocean. The Southern Subtropical Convergence (SSTC) is an area of high productivity, where elevated chlorophyll concentrations are clearly visible in satellite images compared to the surrounding subtropical gyre and ACC (Figure 3.1). It is thought that the elevated productivity may result from the mixing of N limited subtropical waters (Dugdale and Goering, 1967; Eppley et al., 1979) with iron (Fe) limited subantarctic waters. The provision of N and Fe during mixing at the SSTC is attributed for the enhanced productivity. This is a dynamic region and conditions are subject to seasonal movement of the front which poses a challenge in constraining the importance of different processes. Nutrient replete waters are brought to the surface of this region via subantarctic surface water masses from the Southern Ocean; this provides the macronutrients necessary for primary production. These waters meet relatively nutrient-poor subtropical water masses stripped of their nutrients in their transport South and West, creating a complex nutrient regime (Ito et al., 2005). Although this region is very productive, the mechanisms which supply fixed N to the surface have not been studied in great detail. It is not known whether the subtropical waters are principally supplied by fixed N from the subantarctic or via other N cycling processes. If the relative fractions of sources and sinks in the fixed vs recycled pools were known, this could be resolved.

Investigating and quantifying the cycling of nitrate ($\text{NO}_3^-$) through shipboard measurements in the open ocean is made difficult by the inherent temporal and spatial variability. This task is further complicated due to uncertainties from using model derived circulation estimates. Isotopic measurements, on the other hand, can produce integrated signatures of dynamic processes which help to overcome the
constraints of snapshot measurements and produce a more informative view of the processes that occur in the marine environment (Sigman et al., 2009b; Rafter et al., 2012). In this way, nitrogen and oxygen isotopes of nitrate can be used as tracers for N cycling processes. The isotope ratios within nitrate ($^{15}/^{14}$N and $^{18}/^{16}$O) are sensitive to fractionation during biogeochemical N cycling processes. Additionally, N and O isotope of NO$_3^-$ can be used to estimate N inputs and outputs and to identify the origin and history of water masses (Sigman et al., 2000; Deutsch et al., 2004). Isotope ratios are measured relative to a reference (AIR, VSMOW) and are expressed as a delta notation ($\delta^{15}$N vs AIR (‰) = $(R_{\text{sam}}/R_{\text{std}} - 1) \times 1000$, $\delta^{18}$O vs VSMOW (‰) = $(R_{\text{sam}}/R_{\text{std}} - 1) \times 1000$).

One of the principal N cycling processes which fractionates $\delta^{15}$N$_{NO3}$ and $\delta^{18}$O$_{NO3}$ is the consumption of NO$_3^-$ by phytoplankton. The $\delta^{15}$N and $\delta^{18}$O of surface water NO$_3^-$ increases as NO$_3^-$ is progressively utilized by phytoplankton, through the preferential consumption of $^{14}$N and $^{16}$O (Altabet, 1991; Altabet and Francois, 1994). This process and other N cycling processes can be described by Rayleigh fractionation systematics (Mariotti et al., 1981). NO$_3^-$ utilization by phytoplankton in an environment where there is no resupply of nutrients follows Rayleigh fractionation systematics for a closed system, with $\delta^{15}$N and $\delta^{18}$O falling on a fractionation trend for its isotopic effect ($\epsilon$) (Granger et al., 2004). As there is no resupply of nutrients, $\delta^{15}$N$_{NO3}$ and $\delta^{18}$O$_{NO3}$ become increasingly enriched following an isotope enrichment trend dependent on the isotope effect (See Chapter 1).

This mechanism can be used as an integrative measure to estimate the biologically available nitrogen fluxes to surface waters (Sigman et al., 1999). The isotope effect of NO$_3^-$ utilisation in the Southern Ocean has been used to investigate changes in productivity over glacial, interglacial cycles highlighting its importance as a geochemical proxy in palaeo studies (Francois et al., 1997, Sigman et al., 1999, Sigman and Boyle, 2000, Karsh et al., 2003). In the modern Southern Ocean, the process of NO$_3^-$ utilisation can be also used to trace the progressive consumption of NO$_3^-$ from the Polar Antarctic Zone (PAZ) to the Sub Antarctic Zone (SAZ). The understanding of the fractionation of NO$_3^-$ has allowed the importance of mixing processes to be inferred in the formation of the Sub Antarctic Mode Water (SAMW)
(Sigman et al., 2000; Difiore et al., 2006). These reactions can therefore be used to trace the consumption of $\text{NO}_3^-$ in the mixed layer, but also other $\text{NO}_3^-$ isotope fractionating processes such as denitrification and ammonium oxidation.

When $\text{NO}_3^-$ is fully consumed within the mixed layer, the particulate N produced should have the same isotopic composition as $\text{NO}_3^-$ supplied to the surface waters. Deviations away from modelled processes of N fractionation can provide information about different sources of N supplied to the mixed layer and the role of N recycling processes. As diazotrophs uptake $\text{N}_2$, no fractionation occurs therefore values of -2 to 0‰ are typically found for $\delta^{15}\text{N}$ of particulate (PN) of $\text{N}_2$ fixation origin (Carpenter et al., 1997). This leaves remineralised $\text{NO}_3^-$ sourced from $\text{N}_2$ fixation relatively depleted in $^{15}\text{N}$ compared to $\text{NO}_3^-$ sourced from upwelling or lateral mixing into the surface layer (subsurface $\delta^{15}\text{N}_{\text{NO}_3}$ typically ~5‰). Atmospheric deposition of fixed N typically has values between -4 and 0‰, and therefore also can be identified in comparison to subsurface sources already present in the water column (Morin et al., 2009). The use of $\text{NO}_3^-$ isotopes as integrative tracers of N cycling processes allow the relative importance of different inputs of fixed N to be assessed away from their source. Even without the presence of $\text{N}_2$ fixing organisms in the water column, the isotopes of $\text{NO}_3^-$ provide an integrated measurement of the proportion of $\text{NO}_3^-$ that was supplied from either subsurface $\text{NO}_3^-$ or new N sources. This therefore gives insight that has not been possible in previous studies of the South Atlantic.

The O isotopes of $\text{NO}_3^-$ give additional insights to N cycling processes, a result of N and O atoms being sourced from different molecules when $\text{NO}_3^-$ is formed. When fixed N is oxidized back into $\text{NO}_3^-$, N is sourced from the fixed N pool (organic matter and $\text{NH}_4^+$), which is subsequently converted to $\text{NO}_2^-$ and $\text{NO}_3^-$, therefore isotopically it is dependent on the $^{15}\text{N}$ of the fixed N source. $\delta^{18}\text{O}_{\text{NO}_3}$ is principally sourced from O atoms within $\text{H}_2\text{O}$ and a small proportion from $\text{O}_2$, which is relatively homogeneous throughout the ocean (Buchwald et al., 2012). The newly formed $\delta^{18}\text{O}_{\text{NO}_3}$ therefore loses any signature of N cycling processes which the $\delta^{15}\text{N}_{\text{NO}_3}$ would retain. This fundamental difference allows their coupled measurement to delineate $\text{NO}_3^-$ production and consumption. As the processes of nitrification
coupled with many N cycling processes such as N\textsubscript{2} fixation and redox cycling deviate for 15\textsuperscript{N} more than 18\textsuperscript{O}, this deviation can be used to quantify their relative importance compared to the processes which consume NO\textsubscript{3}\. This deviation in dual isotope measurement \(\Delta(15\text{-}18)\) (defined here as \(\delta^{15}\text{N}_{\text{NO}_3} - \delta^{18}\text{O}_{\text{NO}_3}\)) therefore can be used to constrain internal NO\textsubscript{3} cycling further than \(\delta^{15}\text{N}\) alone (Sigman et al., 2009) (Sigman et al., 2009b).

This paper presents NO\textsubscript{3} isotope data from the UK GEOTRACES transect of the South Atlantic at 40\textdegree S and is used to help unravel and identify nutrient cycling that occurs in this region. The supply of N to the mixed layer across the subtropical front is investigated and contrasting N cycling processes north and south of the front are revealed. South of the front, lateral supply of nutrients from the subantarctic fuel primary production. A high availability of N and Fe limitation, results in a low biological demand for N and a build-up of residual NH\textsubscript{4}\textsuperscript{+} in the upper water column. In the subtropical water masses, recycled nutrients are the dominant supply to oligotrophic surface waters. This study reveals the build-up of fixed N from N\textsubscript{2} fixation within subtropical water masses, which provides a significant amount of fixed N to the South Atlantic thermocline.
3.3 Methods

Water samples were collected as part of the UK GEOTRACES transect of the South Atlantic at 40°S. The full transect was completed on cruise JC068 on the RRS James Cook between December 2011 and February 2012. Nitrate and nitrite concentrations were determined using an AA III segmented-flow Auto Analyser (Bran & Luebbe) following colorimetric procedures (Woodward and Rees, 2001). Water samples for NO$_3^-$ isotope analysis were collected from the stainless steel rosette. Seawater was filtered through an Acropak filter (0.45 µm) into acid clean 60 ml Nalgene bottles and frozen at -20 °C. The isotopic composition of NO$_3^-$ was determined by the Denitrifier Method (See Chapter 2) (Sigman et al., 2001; Casciotti et al., 2002). All samples were corrected using international reference standards N3, USGS-32, USGS-34 and USGS-35 (Bohlke et al., 2003) and expressed in delta notation (δ$^{15}$N %o vs AIR = $R_{sam}/R_{std}$ -1 x 1000, δ$^{18}$O %o vs VSMOW = $R_{sam}/R_{std}$ -1 x 1000). Isotopic values stated are from at least duplicate analyses with one standard deviation for δ$^{15}$N at ± 0.2‰ and δ$^{18}$O at ± 0.5‰.

Particulate samples were collected onto muffle furnace (at 450 °C for four hours), pre weighed GF/F microfibre filters (0.7 µm pore size, 25 mm diameter). Water was collected from the CTD in the surface 400 m, 2-4 litres were taken from the high chlorophyll surface waters and ~10 litres from deeper waters. Eight depths were sampled and pressure filtered simultaneously using a compressor (at ~10 psi) and an 8-way manifold system. Once the total volume for each depth was filtered, filters were rinsed with Milli-Q, extracted from the filter holder, placed in labelled aluminium foil and dried at 50 °C for ~12 hours. Once dried, filters were folded and placed in ziplock bags and frozen at -20 °C. Each filter was wetted with Milli-Q, fumed with 70% v/v HCl for 48 hours in a desiccator to remove carbonates, dried at 50 °C and then folded into tin capsules. Organic nitrogen content on the filter was first determined using a Carlo Erba instrument NA2500 elemental analyser. PACs and acetanilide standards were used for sample calibration, and final PN concentrations were calculated using SPM content. The isotopic composition of particulate nitrogen was measured in line with EA by continuous flow IRMS, through the directly coupled VG Prism III mass spectrometer.
Figure 3.1 Satellite images of Chlorophyll concentrations from September 2011 to February 2012. The enlarged map shows a composite of chlorophyll concentrations from the month of sample collection (January 2012). Sampling stations are outlined and colour coded to show whether the station captures the waters north (subtropics) or south (subantarctic) of the front (Red=north, Blue=south, Green= Rio Plata). The subtropical and subantarctic water masses are identified as AC=Agulhas Current, SACW=South Atlantic Central Water, BC=Brazil Current, MC=Malvinas Current and SASW= Sub Antarctic Surface Water. Figure adapted from Browning et al. (2014).
3.4 Results

3.4.1 Physical Oceanography

Elevated chlorophyll concentrations are evident from satellite images across the South Subtropical Convergence (SSTC) region of the South Atlantic (Figure 3.1). The convergence moves south from austral spring to summer (as evidenced by chlorophyll concentrations). At the time of sampling (late December to early February 2012) our transect captured water masses both north and south of the front (Figure 3.1). The water mass characteristics across the transect are identified in Figures 3.2 and 3.3. During winter a deep surface layer with uniform temperature and salinity forms the Subantarctic Mode Water (SAMW) in the Subantarctic Zone (SAZ). This water mass sinks below the SSTC, and is identified at the base of the profiles at ~500 m. The SAMW is identified with a density of 26.8-27 kg m\(^{-3}\) and salinities of 34-34.5 psu. The SAMW which forms at the subantarctic surface has NO\(_3\) of 17-30 µM. Above the SAMW, the surface layer at the Atlantic subtropical front consists of five main surface water masses, creating a complex system of water dynamics. Subantarctic surface waters (SASW) flow northward by Ekman transport and bring nutrients to the subtropical front surface layer. Stations located south of the subtropical front within the SASW have lower temperatures, lower salinities (34.5 to 34.7 psu) and higher nutrient concentrations (Figures 3.2 and 3.3).

South Atlantic Central Water (SACW) formation occurs in the confluence zone of the Brazil and Falkland (Malvinas) current and is transported within the South Atlantic current towards Africa. The water properties of the SACW range from 5-20 °C and 34.3-36.0 psu and are located towards the centre of the transect to the north of the subtropical front (Figure 3.2). The Brazil Current forms the western limb of the SACW, it is identified as more saline and with higher temperatures than the SACW, in this transect salinities up to ~36.7 psu are observed. Slightly lower salinities separate the Brazil Current from the SACW. This identifies the Brazil-Malvinas Confluence (BMC) where subantarctic waters are transported north along the west coast of southern South America and meet the Brazil Current (Figure 3.3). The furthest west station (24) is located on the continental shelf region and is therefore heavily influenced by the outflow of the Rio Plata; as identified by the lower
salinities (28-33 psu). The Agulhas Current flows southwards along the east coast of Africa and transfers Indian subtropical waters to the South Atlantic Ocean. As the current reaches the tip of the continental shelf, it turns west. On interaction with western boundary currents and the Southern Ocean, the current retroreflects and large energetic mesoscale eddies are spun off. Some of these eddies are shed into the Cape basin but others form the Agulhas return current. The Agulhas Current is identified here with salinities up to 35.3 psu on the eastern edge of the transect (Figures 3.2 and 3.3).

Figure 3.2 Temperature and salinity properties in the surface 500 m across 40°S. Colours denote nitrate concentrations. The core of each water mass is identified: AC=Agulhas Current, SACW=South Atlantic Central Water, BC=Brazil Current, MC=Malvinas Current and SASW=Subantarctic Surface Water. The Rio Plata influenced samples have much lower salinities than the open ocean samples and are highlighted in grey.
Figure 3.3 Sections of a. Salinity, b. Nitrate, c. Ammonium and d. Nitrite from 20°E to 60°W at 40°S. Relative homogeneity of salinity and nitrate is observed in the underlying SAMW. High variability in salinity and nitrate is observed in the surface 300 m with the convergence of subtropical and subantarctic water masses. A maximum in NH$_4^+$ and NO$_2^-$ is identified in the subantarctic water masses at ~60-100 m; no NH$_4^+$ is evident in the subtropical water masses. SAMW=Sub Antarctic Mode Water, SASW= Subantarctic Surface Water, AC = Agulhas Current, SACW = South Atlantic Central Water and BC = Brazil Current.
3.4.2 Nutrient cycling

The SAMW core is identified at 500 m, by low Si:N concentrations (Sarmiento et al., 2004), where NO$_3^-$ concentrations range between 17-30 µM and NO$_3^-$ decreases towards the surface (Figure 3.2 and 3.3). The thermocline waters (between 300 m and 100 m) have variable nutrient concentrations. Lower concentrations are identified at the base of subtropical water masses, from greater mixing with the low NO$_3^-$ subtropical thermocline (Figure 3.3). Higher concentrations are identified at the base of the SASW and Malvinas Current (Figure 3.3), as less subtropical water reaches south of the front. NO$_3^-$ concentrations are very low in the surface waters (0-50 m) north of the subtropical front with values typically between 0-2 µM. South of the front NO$_3^-$ concentrations range between 4-8 µM, with the highest concentrations at the core of the SASW. To explore the nutrient characteristics of the region further the NO$_3^-$ concentrations can be normalized to PO$_4^{3-}$ using the tracer N*, defined as $N^* = NO_3^- - 16 (PO_4^{3-})$ (Gruber and Sarmiento, 1997). This tracer assumes that uptake and regeneration of N follows the Redfield ratio of 16:1, and that deviations away from this ratio may indicate whether N$_2$ fixation or denitrification have altered the nutrient stoichiometry. The subtropical surface waters typically have higher N* concentrations compared to the subantarctic waters, ranging between -2 and 0 µM compared to the subantarctic waters of -2 and -4 µM (Figure 3.4). Although the subtropical waters have slightly elevated N* values, they are much lower than values that observed in the North Atlantic thermocline.

Nitrite (NO$_2^-$) and ammonium (NH$_4^+$) concentrations were low throughout most of the transect. The highest concentrations are located at between 50-100 m, at the base of the mixed layer. An NH$_4^+$ maximum is present in the subantarctic waters, where salinities were below ~35.2 psu, with concentrations of up to ~600 nM at 60 m. The NO$_2^-$ maximum coincides with the same region, with values up to ~0.6 µM, NO$_2^-$ was present up to 0.3 µM in all stations at 60-100 m, but was consistently below 0.1 µM in the rest of the transect. The NO$_2^-$ maximum was both smaller spatially and in concentration in the western basin in comparison to the eastern basin. No NH$_4^+$ was measured in the subtropical water masses. The maximum of NH$_4^+$ and NO$_2^-$
identified in the SASW, may suggest a low efficiency of N recycling, partly due to the higher supply of NO$_3^-$ to this region.

Figure 3.4 Depth profiles of a. $\delta^{15}$N$_{NO3}$, b. NO$_3^-$, c. $\delta^{18}$O$_{NO3}$ and d. N* for each station across the transect. The salinity of each sample is shown with colour.
Figure 3.5 Sections of a. $\delta^{15}\text{N}_{\text{NO}_3}$ b. $\delta^{18}\text{O}_{\text{NO}_3}$ c. $\Delta(15-18)$ (calculated here as $\delta^{15}\text{N}_{\text{NO}_3} - \delta^{18}\text{O}_{\text{NO}_3}$) and d. $\delta^{15}\text{N}_{\text{PN}}$. Higher $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ are observed principally in the top 100 m, and in particular in the subantarctic water masses. A minimum in $\Delta(15-18)$ is observed between 100-200 m, with the lowest values observed in the subtropical water masses.
3.4.3 Nitrate isotopes

At 500 m salinity and NO$_3^-$ are relatively uniform and characteristic of the SAMW. The isotopic composition similarly reflects this homogeneity, with a range of 5-7‰ for $\delta^{15}$N$_{NO_3}$ and 2-4‰ for $\delta^{18}$O$_{NO_3}$ (Figure 3.5c). It is important to note that the $\delta^{15}$N/NO$_3^-$ for the SAMW in Rayleigh space does not fall on a 5‰ trajectory compared to the underlying Antarctic Intermediate Water (AAIW) and Upper Circumpolar Water (UCDW) from which it has formed. This observation is thought to be a result of mixing in formation regions or recycling of nutrients (as described in Chapter 4). Towards shallower depths, $\delta^{15}$N$_{NO_3}$ and $\delta^{18}$O$_{NO_3}$ increase through the thermocline, with the sharpest increase identified in the mixed layer. A higher enrichment in both $\delta^{15}$N$_{NO_3}$ and $\delta^{18}$O$_{NO_3}$ is identified in the SASW compared to the rest of the transect (Figure 3.5). Concentrations of NO$_3^-$ decrease from 500 m to the surface, however a corresponding increase in $\delta^{15}$N$_{NO_3}$ and $\delta^{18}$O$_{NO_3}$ is not observed until ~100 m (Figure 3.4). This suggests that NO$_3^-$ utilisation is not the sole process occurring in this region. Figure 3.6 describes the overall NO$_3^-$ isotope distributions against the natural log of NO$_3^-$ (Rayleigh space), showing that there are a number of processes working to fractionate the isotopes away from purely Rayleigh fractionation systematics for NO$_3^-$ utilisation. Compared to the assumed Rayleigh effect of NO$_3^-$ consumption in the Southern Ocean (5‰), as NO$_3^-$ decreases from the core of the SAMW through the thermocline, the samples at shallower depths do not all follow this predicted trend (Figure 3.6).

The thermocline waters at 200 m are identified in Figure 3.6 with black outlines. It is evident that the samples with the lowest salinities have similar characteristics to the SAMW compared to the samples with higher salinities. As salinity increases across 40°S (and as such the proportion of subtropical NO$_3^-$), NO$_3^-$ decreases and $^{15}$N remains relatively constant or, at salinities above 35.2 psu, moderately decreases. With increasing salinity, $\delta^{18}$O$_{NO_3}$ either stays at a similar value or increases modestly, though with larger variability identified.
Figure 3.6 The dual isotopes of nitrate plotted in Rayleigh space. Colour denotes salinity and samples highlighted with black circles are from 200 m. a. δ¹⁵N\text{NO}_3\text{ with changes in ln(NO}_3^-), b. δ¹⁸O\text{NO}_3\text{ with changes in ln(NO}_3^-), and c. δ¹⁸O\text{NO}_3\text{ vs. δ¹⁵N\text{NO}_3}. Arrows represent the direction in which δ¹⁵N\text{NO}_3\text{ and δ¹⁸O\text{NO}_3} should fractionate with different N cycling processes. Black: In nitrate utilization, δ¹⁵N\text{NO}_3\text{ and δ¹⁸O\text{NO}_3} should increase exponentially with nitrate decrease following ε=5‰ (identified as a straight line in a. and b. against ln(NO}_3^-), with a slope=5‰). As both δ¹⁵N\text{NO}_3\text{ and δ¹⁸O\text{NO}_3} are fractionated equally, there is no deviation in c. Purple: As nitrate mixes with nitrate depleted waters, the concentration will decrease without a change in the isotopic value, therefore the purple arrow in a. and c. denotes how samples would move towards 0 without a change in y. In c. mixing would not change δ¹⁵N\text{NO}_3\text{ or δ¹⁸O\text{NO}_3} and therefore Δ(15-18). Red: Arrows represent how the remineralisation of light δ¹⁵N\text{NO}_3\text{ would affect samples. In a. δ¹⁴N would decrease along a mixing line which would be determined by the concentration of the source. In c. Light δ¹⁴N would cause the Λ(15-18) to decrease and thus samples to fall above the thick grey dashed line.

δ¹⁵N\text{NO}_3\text{ and δ¹⁸O\text{NO}_3} within the mixed layer of the SASW follow an isotope effect of ~5‰ from the SAMW (Figure 3.6). However thermocline data fall away from this trend as the NO}_3^- is diluted with subtropical waters. The mixed layer samples have a
higher salinity than the SAMW (Figures 3.3 and 3.5), providing evidence for mixing. It is therefore more accurate to use the thermocline data as a starting point for NO$_3^-$ utilization so as not to underestimate the fractionation (Figure 3.6). For the purposes of this study I compare the mixed layer salinity to subsurface salinity to identify the initial NO$_3^-$ and $^{15}$N. Here the mixed layer is a mixed component of the SAMW and subtropical thermocline, which is similar to the salinity at 200 m, which I use as the initial point for the process of NO$_3^-$ assimilation. The $\delta^{15}$N$_{NO3}$ and $\delta^{18}$O$_{NO3}$ from stations south of the front are more enriched at the same NO$_3^-$ concentration and follow Rayleigh systematics when plotted against the natural log of NO$_3^-$ with an isotopic effect of ~7-9‰ (Figure 3.7 and 3.8). The stations north of the front have lower $^{15}$N for a given nutrient concentration and demonstrate open system dynamics as opposed to Rayleigh “closed” systematics. In most stations the $\delta^{15}$N$_{NO3}$ and $\delta^{18}$O$_{NO3}$ still increase to the surface, but the degree of fractionation decreases with increased salinity, a signature for the dilution of $\delta^{15}$N$_{NO3}$ and $\delta^{18}$O$_{NO3}$ signatures.

Figure 3.7 $\delta^{15}$N$_{NO3}$ and $\delta^{15}$N$_{PN}$ plotted in Rayleigh space, samples are separated into those north and south of the front. A. $\delta^{15}$N$_{NO3}$ = red, $\delta^{15}$N$_{PN}$ = yellow, b. $\delta^{15}$N$_{NO3}$ = dark blue and $\delta^{15}$N$_{PN}$ =light blue. Model estimates for an isotope effect of 5‰ are added to each plot with trajectories for the fractionation of reactant and product by the process of nitrate utilization.

In Figure 3.6c the deviations in the two isotope systems away from a 1:1 fractionation trend are identified. These deviations are also identified in the $\Delta$(15-18) distributions across the transect in Figure 3.5. The $\Delta$(15-18) profiles for 40°S, are relatively constant between 500-300 m at ~2.5-3.5‰ and comparable to intermediate
waters from Pacific Ocean (Rafter et al., 2013), falling close to the dashed line in Figure 3.6c. The Δ(15-18) decreases by 200 m which suggests that remineralisation of organic matter has caused the two isotope systems to deviate from one another. In all parts of the transect, this deviation is from lower δ¹⁵NNO₃ compared to δ¹⁸ONO₃, which subsequently leads to a low Δ(15-18). In Figure 3.5, it is identified that this Δ(15-18) deviation has a minimum at 100 m across the transect with values of ~0‰ in subtropical waters and ~1‰ in subantarctic waters.

3.4.4 Suspended particulate nitrogen

Within the Brazil Current and Agulhas Current, particulate nitrogen is typically between 1-3‰. The SACW signatures are considerably heavier at ~6-8‰ at 100 m; and slightly more enriched than the samples at the surface, which may suggest preferential remineralisation of lighter N. The SASW surface waters to the south of the front have values typically between 0-5‰. Between 200-500 m averaged suspended particulates have values of ~6.63 ± 1.62‰. Figure 3.7 shows the relationship between the δ¹⁵N of suspended particulates and the NO₃⁻ concentrations. This approach can be used to identify the processes which are fractionating N isotopes during primary production. Here samples with salinities >35 psu (red) were separated from samples with lower salinities (blue). In Rayleigh space, samples from south of the front fall on the trajectory of the ¹⁵N reactant line for a closed system (ε =5‰), when the assumed initial value is taken to be the thermocline at 200 m. The δ¹⁵NPN has more variability but lies close to the integrated product for a closed system. The higher salinity δ¹⁵NNO₃ data tend to fall much lower than the ¹⁵N reactant line for a closed system with a larger range and can be better described by the open system fractionation trend (Figure 3.7). δ¹⁵NPN north of the front also falls lower than the open system product, but follows the same trajectory, perhaps suggesting a source of lighter ¹⁵N to the subtropical waters which will be explored further in the discussion.

3.4.5 Input of fixed N from the Rio Plata

To assess the input of NO₃⁻ from the Rio Plata into the Western Atlantic I assess the different signatures found in the depth profiles on the western boundary. Station 24
has low salinities (28-33.5 psu) and contrasting nutrient characteristics to the samples further offshore. Although the NO$_3^-$ concentration for Stations 24-21 are very low, the high phosphate concentrations observed at Station 24 result in very distinct N* concentrations. Figure 3.4 shows the very low N* concentrations for Station 24 and samples between 50-100 m in Station 22. The rest of Station 22 (0-50 m and 100-200 m) has higher salinities and N* concentrations typical of the Brazil Current, suggesting its dominant influence in the surface waters. The samples between 50-100 m show that the waters from the Rio Plata are being transported down from the surface as they leave the continental shelf, which could be due to the influence of turbidity, and high concentrations of suspended particulates. Rio Plata is not a dominant supply of NO$_3^-$ to the Western Atlantic as seen in NO$_3^-$ concentrations in Station 24. However, it is a source of P and Fe and hence can affect the productivity of this region. In particular, P and Fe are necessary requirements for the growth of N$_2$ fixers and therefore the influence of Rio Plata can influence this process. This is supported by biological data from Station 24 where *Trichodesmium* were recorded (Tom Browning, personal communication.)

Although the shelf region has low nitrate concentrations, other sources of fixed N may affect $\delta^{15}$N across this region. Lighter $^{15}$N signatures in the subtropical water masses may result from a sedimentary shelf source and thus should be explored in more detail. Sources of PN or DON could provide such a source. From our isotopic analyses of $\delta^{15}$N$_{PN}$ from the Rio Plata region, the low salinity samples measured at Stations 24 and 22 fall between a range of 5.5 and 9.8‰ (n=4), and thus are more enriched than the light signatures identified in the Brazil Current and Agulhas Current. DON has a long residence time within the ocean of many months to years and can persist for long timescales. Recent work into the $\delta^{15}$N of DON within the Pacific and Atlantic has found $\delta^{15}$N$_{DON}$ to be elevated by ~4‰ in comparison to PN, therefore suggesting that this may not be a source of low $^{15}$N to the continental margins, but may in fact retain elevated $^{15}$N signatures (Knapp et al., 2011). This could be further explored in future work to identify the $\delta^{15}$N of DON, but our best isotopic constraints suggest that this is not a factor influencing the $\delta^{15}$N of nitrate and particulate N in the subtropical regions of the transect.
3.5 Discussion

The biogeochemical cycling of N across the productive SSTC will be investigated in terms of the supply of fixed N to the surface waters. In Figures 3.4 and 3.6, it is evident that the fractionation of $\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$ varies in the subantarctic and subtropical sections of the transect. In this discussion, the mechanisms behind the distribution of $\delta^{15}N_{NO_3}$, $\delta^{18}O_{NO_3}$ and $\Delta(15-18)$ across the transect will be discussed. In Figure 3.6, the isotopic distribution of N and O is identified against NO$_3^-$ concentration and in N:O space. From the SAMW to the mixed layer most samples become increasingly enriched in $\delta^{15}N$ and $\delta^{18}O$ as NO$_3^-$ concentrations decrease. The samples in the mixed layer of the SASW fall on a fractionation trend of 5% from the SAMW, although the thermocline waters fall away from this trend. The salinity changes across the transect show mixing that dilutes the fractionation away from a NO$_3^-$ utilisation trend (purple arrows in Figure 3.6). In N:O space (Figure 3.5 and 3.6c), the samples become decoupled at 100-200 m, with $\delta^{15}N$ identified as lower than $\delta^{18}O$. This observation requires regeneration processes to be taking place that would add lower $\delta^{15}N$ compared to $\delta^{18}O$. Initially the processes which consume NO$_3^-$ will be discussed, next the processes of physical mixing and thirdly the sources and recycling of NO$_3^-$ will be discussed. The isotopic constraints will then be used to quantify the supply of fixed N to the surface from different sources.

3.5.1 Consumption of fixed N by phytoplankton

3.5.1.1 Subantarctic water masses

The enrichment of $\delta^{15}N$ and $\delta^{18}O$ as NO$_3^-$ decreases, is much lower than the isotope effect of denitrification ($\varepsilon =25-30\%$) (Figure 3.6). This and the highly oxygenated waters across the region rule out denitrification processes in fractionating the two isotopic systems. Instead the process of NO$_3^-$ consumption by phytoplankton is investigated. If NO$_3^-$ consumption occurs with a constant isotopic effect and there is no resupply of nutrients throughout the season, then the process of NO$_3^-$ consumption can be explained using Rayleigh fractionation kinetics (Mariotti et al., 1981). As NO$_3^-$ is consumed by phytoplankton in surface waters, the residual pool of nutrients becomes increasingly enriched in $\delta^{15}N$ and $\delta^{18}O$ as the lighter isotope is preferentially consumed. Laboratory cultures and field observations from the
Southern Ocean, where Rayleigh systematics are observed, have found an isotopic effect of $\varepsilon=5.9\%$ for both isotopes ($^{15}\varepsilon=^{18}\varepsilon$) (Sigman et al., 1999; Altabet, 2001; Karsh et al., 2003; Granger et al., 2004). Recent studies of the Sub Antarctic have found the isotopic effect to be higher in the Sub Antarctic Zone (SAZ) ($\varepsilon=8.9\%$) in comparison to the Polar Antarctic Zone (PAZ) ($\varepsilon=5\%$), with a deeper mixed layer and thus light limitation, being inferred as the cause of this higher fractionation (DiFiore et al., 2006; DiFiore et al., 2010). In other regions such as the Azores Front (Bourbonnais et al., 2009), the subtropical North Atlantic (Knapp et al., 2005; Knapp et al., 2008) and HOT (Hawaiian Ocean Time-Series) (Casciotti et al., 2008), NO$_3^-$ is limiting, and any available N (normally NH$_4^+$) is quickly consumed. In these cases and for much of the subtropical regions, a Rayleigh system is not suitable to describe the environment as mixing, remineralisation and very low N concentrations in the mixed layer cause samples to deviate from this trend.

If NO$_3^-$ consumption is the dominant effect in the mixed layer of the SASW, the N and O isotopes should not deviate from one another. This is reflected in the $\Delta(15-18)$ signatures within the SASW mixed layer which is 2-3\%, similar to the SAMW. The isotopic fractionation is also similar for both isotopic systems, as shown in Figure 3.8. This supports NO$_3^-$ assimilation in the mixed layer of the SASW being dominant.
over the effects of NO$_3^-$ regeneration. Figure 3.7 shows the change in both NO$_3^-$ and particulate N with decreasing NO$_3^-$ concentration, where the “south” samples lie close to closed system fractionation. NO$_3^-$ concentrations remain replete in this section of the transect and other nutrients such as iron are likely to be limiting productivity (Browning et al., 2014). The biological requirement for active recycling and transport of new fixed N into the surface layer is therefore not required. This supports the reasoning that NO$_3^-$ is supplied to the surface layer in winter mixing with the thermocline and consumed by phytoplankton over the course of the season. The remineralisation of this organic matter is not being resupplied to the mixed layer at a similar rate to NO$_3^-$ being consumed.

The cross frontal transport of NO$_3^-$ to the SAZ from the south Polar Antarctic Zone (PAZ) has been identified in both isotope data (DiFiore et al., 2006) and TS data (Rintoul and Trull, 2001). Intermediate and surface waters of the subantarctic are ultimately sourced from the ACC and therefore should have initial concentrations and isotopic characteristics close the UCDW (Rafter et al., 2013). In comparison to the UCDW, the SAMW has a small increase in $^{15}$N for a given decrease in NO$_3^-$ (DiFiore et al., 2006; Sigman et al., 2000) (See also Chapter 4). This mechanism is explained by the winter vertical mixing of Sub Antarctic waters and underlying thermocline water, which exchanges with the subtropical surface waters. This process dilutes the subantarctic NO$_3^-$ without causing $^{15}$N enrichment from NO$_3^-$ utilisation (DiFiore et al., 2006). If there is no resupply or dilution of NO$_3^-$ during its consumption by phytoplankton, the isotopic effect ($\varepsilon$) or fractionation that occurs within the substrate pool can be measured. If the initial NO$_3^-$ concentration is known, $\delta^{15}$N and $\delta^{18}$O should follow a straight line vs ln(NO$_3^-$), and the slope (multiplied by -1) should provide an estimate for the isotopic effect (Figure 3.8). If the NO$_3^-$ concentration of the initial pool is not known from which NO$_3^-$ consumption proceeds, this can lead to an under or overestimation of the isotope effect, as this would change the gradient of the slope. If the SAMW (with lower salinities and higher nitrate concentrations than the SASW mixed layer), is used as the initial conditions for NO$_3^-$ consumption within our dataset, this may lead to an under representation of N fractionation by phytoplankton. In this frontal region there is
interaction between two very contrasting nutrient regimes. This highlights that truly closed system dynamics are not fully applicable where there is mixing occurring. To measure the isotopic effect I test this, by changing the initial values from the SAMW, to the thermocline to the mixed layer to calculate the differences in estimates (Figure 3.8).

In doing so, there is an increase of 1.2‰ and 1.3‰ in our estimations both for $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ when using mixed layer data. We adopt initial values of <300 m to account for this underestimation and our estimates of the isotope effect of NO$_3^-$ consumption fall between 5.3‰ and 6.2‰ for $\delta^{15}\text{N}_{\text{NO}_3}$ and 5.4‰ and 6.8‰ for $\delta^{18}\text{O}_{\text{NO}_3}$. The results of this work show that biological N uptake with an isotopic effect of 5.3-6.8‰ within the mixed layer is observable in surface NO$_3^-$ at the subtropical front. Culture studies have found that diatoms, which are abundant in the Southern Ocean, have a typical $\varepsilon$ of 5‰ (Granger et al., 2010). The coccolithophore *Emiliania huxleyi* was found to be the dominant species identified south of the front, with this species, the isotopic effect has been found to be relatively constant, even in changing nutrient conditions, with estimates ~4-5‰ (Waser et al., 1998). Our data support this, with a similar isotope effect albeit slightly higher.

A comparison of the isotopic effect of NO$_3^-$ utilization through the Southern Ocean found the isotopic effect to be higher in the Sub Antarctic Zone (SAZ) ($\varepsilon=8-9$‰) in comparison to the Polar Antarctic Zone (PAZ) ($\varepsilon=5$‰) (DiFiore et al., 2010). It has been found that diatom species such as *T.weissflogii* have elevated $\varepsilon$ in low light conditions, compared to limitations by Fe or temperature (Needoba and Harrison, 2004). The dominant driver of NO$_3^-$ isotope fractionation is by the process of NO$_3^-$ reduction. It has been hypothesised that in light limitation NO$_3^-$ uptake increases compared to NO$_3^-$ reduction in the hope that conditions will change to higher light availability in a turbulent and changing ocean (Needoba et al., 2004). This was suggested as a mechanism for the observed correlation between Southern Ocean estimates of $\varepsilon$ and mixed layer depth (DiFiore et al., 2010). Deep mixed layer depths are observed in the SAZ, compared to the OAZ and PAZ, which may account for a change in isotopic effect. The deep SAZ mixed layer observed in spring is driven by strong wind stress and relatively weak water column stratification. From recent work,
it has been found that Fe limits rates of productivity across this region, which suggests that light limitation is unlikely to have a dominant effect (Browning et al., 2014). In this study, the mixed layer depth is ~55 m in the subantarctic waters; which is lower than the observed mixed layer depths of Difiore et al. (2009). This contrast between the two studies may account for the differences in the isotope effects of nitrate consumption. Although field observations have suggested high isotope effects within the subantarctic, our results suggest that the fractionation by phytoplankton is fairly consistent in the Southern Ocean. I conclude that the isotope effect within the far reaches of the SASW is within current estimates for the full Southern Ocean and that light limitation does not have a dominant effect on our estimates. This difference in SAZ isotope effects may result from different species present or differences in the physical conditions (i.e. mixed layer depth). The discrepancies between recent works in modern N isotope studies highlight the need for further work to understand the processes which may lead to these changes in estimates. The use of N isotope fractionation in sediments is a powerful palaeoproxy to determine the extent of nitrate utilisation in the past (Martinez-Garcia et al., 2014). This proxy is reliant on the isotopic systematics of nitrate consumption. It is therefore important that the isotopic systematics of nitrate consumption in subantarctic regions are resolved.

3.5.1.2 Subtropical water masses
In comparison to the mixed layer of the SASW, samples within the mixed layer of the subtropical water masses fall much further away from the Rayleigh fractionation trend, suggesting that mixing and remineralisation processes are having a dominant effect in these regions (Figure 3.6 and 3.7). NO\textsubscript{3}\textsuperscript{-} concentrations in the mixed layer are low and limit phytoplankton growth; therefore regeneration processes are likely to be important to support productivity. The process of NO\textsubscript{3}\textsuperscript{-} consumption by phytoplankton is being diluted from any significant isotope effect by the increased proportion of subtropical waters of high salinity. These observations suggest a switch from the predominance of preformed NO\textsubscript{3}\textsuperscript{-} in the SASW to remineralised NO\textsubscript{3}\textsuperscript{-} in the subtropics (Figure 3.6). This highlights a change in the mechanisms of primary production, from a nitrate dominant system of new production in the SASW to a
principally regenerated production in the subtropical gyres where NH$_4^+$ is likely to be the dominant fixed N supply to phytoplankton.

### 3.5.2 Mixing of two nutrient regimes

From the deviations observed for $\delta^{15}$N$_{NO_3}$ and $\delta^{18}$O$_{NO_3}$ in Rayleigh space, it is clear that mixing processes are working to dilute the isotope effect of NO$_3^-$ utilisation. In frontal regions, a high degree of mixing is evident as water masses of different densities converge creating a high degree of turbulence. When two water parcels mix and no other N cycling process is occurring, $\delta^{15}$N$_{NO_3}$ and $\delta^{18}$O$_{NO_3}$ should follow a similar mixing line determined by the concentrations and isotopic ratios originating from the cores of the converging water masses (Sigman et al., 2005) (Sigman et al., 2005b). When $\delta^{15}$N$_{NO_3}$ and $\delta^{18}$O$_{NO_3}$ are plotted in Rayleigh space, relatively uniform values are observed for the SAMW (Figure 3.6). From this point there are deviations away from an isotopic effect of 5‰ with increasing salinity; a result of increased low NO$_3^-$ and high salinity subtropical waters. Across most of the transect at depths shallower than 200 m, $\delta^{18}$O and $\delta^{15}$N increase less than expected for NO$_3^-$ utilisation alone (Figure 3.6). Although there is a dilution in this trend for both isotopes, the $\delta^{18}$O increase is more than is observed for $\delta^{15}$N up to 100 m. This is demonstrated with the $\Delta$(15-18) data and the decoupling of the two variables in Figure 3.5 and 3.6c. The dilution and decoupling are reflecting two processes. The dilution reflects the mixing of low NO$_3^-$ waters with subantarctic water thus diluting away from Rayleigh systematics and the low $\Delta$(15-18) indicates sources of remineralised NO$_3^-$.

$\delta^{15}$N$_{NO_3}$ and $\delta^{18}$O$_{NO_3}$ should behave similarly for physical processes therefore there should be no deviation between the two isotope systems. The degree of mixing which dilutes isotopic fractionation trends is clearly less pronounced south of the front. However in the subantarctic waters at 200 m, salinities are higher than expected for the subantarctic waters alone. This shows that the process of winter mixing transfers subtropical waters across the front, increasing the salinity and lowering the NO$_3^-$ concentration. This observation is significant for our understanding of the formation of the SAMW. In Figure 3.6a there is an observed decrease in NO$_3^-$ at 200 m in the SASW from 20 to ~9 µM without any observed
enrichment in $\delta^{15}N_{NO_3}$. As observed in previous studies the SAMW has a low $^{15}N/NO_3^-$ relationship, which requires the addition of low NO$_3^-$ or low $^{15}N$ NO$_3^-$ to its formation. The observed cross frontal mixing of subtropical low NO$_3^-$ waters may supply formation regions of the SAMW. The density increase by mixing high salinity waters has been suggested as one of the causes for the formation of mode waters (Gordon et al., 1989).

At 200 m a decrease in $\Delta(15-18)$ is observed compared to the SAMW, but to a lesser extent than observed at 100 m. Low salinity samples ($<35.1$ psu) do not show a decrease in $^{15}N$ with decreased NO$_3^-$, instead showing either similar isotopic properties to the SAMW or moderate increases (Figure 3.6a). Here mixing is having the dominant effect on these waters. In the samples at the core of the Brazil and Agulhas with the highest observed salinities, $\delta^{15}N_{NO_3}$ decreases to ~4‰ (Figure 3.6a). If mixing NO$_3^-$ deplete surface waters were the only process to be occurring, then the end member values would not be any lower in $^{15}N$ but comparable to the SAMW, only the NO$_3^-$ would decrease and salinity increase. This indicates that at the core of the subtropical water masses, at 200 m, low $^{15}N$ is added via remineralised NO$_3^-$. These data indicate that at 200 m mixing dilutes isotopic signatures over much of the transect, but at the core of the Subtropical waters there is a source of low $\delta^{15}N_{NO_3}$. From 200 m to the surface in most profiles the salinity remains relatively homogeneous suggesting that other factors rather than mixing are working to alter the isotopic signatures in Rayleigh space. Indeed the $\Delta(15-18)$ support this with the largest deviations observed at 100 m, in particular in the higher salinity waters. This suggests that resupply of NO$_3^-$ via nitrification is a dominant process at 100 m in the subtropical waters and to a lesser extent within the subantarctic waters.

3.5.3 Remineralisation of fixed N

Studies to date have found that the processes which consume NO$_3^-$ fractionate both $\delta^{15}N$ and $\delta^{18}O$ with the same isotopic effect (Casciotti et al., 2002; Granger et al., 2004). An anomaly between the two isotope systems therefore has been attributed to N regeneration processes. These processes may work to decrease $\Delta(15-18)$, by the remineralisation of low $^{15}N$ organic matter (Knapp et al., 2008) (Knapp et al.,
Cycling of fixed N in the Atlantic SSTC

2008a), reoxidation of nitrite from redox cycling processes in the subsurface (Sigman et al., 2005; Casciotti and McIlvin, 2007) and recycling processes in NO$_3^-$ replete surface waters (Sigman et al., 2005; Wankel et al., 2007; Rafter et al., 2013). The subtropical front region provides an environment where the recycling of NO$_3^-$ may result in a low $\Delta$(15-18) to occur from a variety of processes. The subantarctic surface is supplied with nutrients transported northwards by Ekman transport from the Southern Ocean. It has been observed that in NO$_3^-$ replete waters, the lighter isotope is preferentially taken up by algae leaving organic matter with a lighter $^{15}$N signature compared to phytoplankton in regions with low NO$_3^-$ (Rafter et al., 2013). To the north of the front, NO$_3^-$ concentrations are limiting, therefore the fixed N of remineralised NO$_3^-$ should represent the integrated product (~5‰). However, if a proportion of the fixed N within these tropical water masses is sourced from N$_2$ fixers or atmospheric deposition, lighter $^{15}$N is added to the fixed N pool, which is propagated into the signatures of remineralised nitrate causing low $\Delta$(15-18).

$\Delta$(15-18) decreases from the SAMW through the thermocline to ~100 m where concentrations are observed as low as 0‰ (Figure 3.5). The deviation in the two isotope systems indicates the production of NO$_3^-$ via internal cycling (Sigman et al., 2009). The lowest $\Delta$(15-18) is within the top 200 m indicating the majority of organic matter produced via photosynthesis is remineralised by 200 m. This is further supported by low PN concentrations below 100 m. At 200 m samples fall away from a 1:1 fractionation trend and a $\Delta$(15-18) minimum is observed at 100 m (Figure 3.6c). In the subtropical waters north of the front $\Delta$(15-18) is lower (1.5-0‰) than the observed $\Delta$(15-18) minimum south of the front (2-1.5‰). Isotopic signatures can be used to decipher the recycling efficiency and sources of remineralised NO$_3^-$ to this region.

**3.5.3.1 Low $\Delta$(15-18) in the SASW**

Surface waters of the HNLC Southern Ocean have high NO$_3^-$ concentrations and as such allow the $^{14}$N NO$_3^-$ to be preferentially consumed in photosynthesis, leading to lighter $\delta^{15}$N signatures in phytoplankton of the Southern Ocean. This process leads to the remineralisation of sinking N from the Southern Ocean surface producing NO$_3^-$ with a lower $\Delta$(15-18) than the source NO$_3^-$. In a recent study, low $\Delta$(15-18) was
identified in subantarctic intermediate waters of ~2‰ at 500 m (Rafter et al., 2013). This was attributed to low δ\textsuperscript{15}N of remineralised nitrate from high nitrate surface waters of the SAZ. Here I find Δ(15-18) as low as 1‰ in the SASW (~100 m). Although the deviations are likely caused from remineralised nitrate, the difference in depth and thus isopycnals of low Δ(15-18) in this study compared to Rafter et al. (2013) suggest different mechanisms. The SAMW is sourced from further south in the Southern Ocean (~50°S), where concentrations of nitrate are much higher, and lead to increased fractionation by phytoplankton consumption. The lighter δ\textsuperscript{15}N produced by surface phytoplankton, therefore occurs further south in the SAZ and should be transported at deeper isopycnals by 40°S (Rafter et al., 2013). Here in the SASW, at 100 m, any remineralised nitrate at this isopycnal was produced in a lower nitrate environment, where less fractionation occurred and thus the Δ(15-18) values derived solely from the nitrate consumption - remineralisation process, should not be as low as observed (Figure 3.9).

The values therefore seem to be lower than previously observed for solely the remineralisation of δ\textsuperscript{15}N from high NO\textsubscript{3}\textsuperscript{-} regions and also located at shallower depths. The Δ(15-18) deviations observed in the Pacific Ocean by Rafter et al.(2013), should be observed at ~500 m in our transect (at 500 m there are decreases of ~0.7‰ from the UCDW to SAMW, likely from this process). To further test that the observed low Δ(15-18) is not solely from the SAZ surface, the change in Δ(15-18) was predicted using estimates of the isotopic fractionation of algal consumption at different nitrate concentrations (Figure 3.9). The isotopic composition of remineralised NO\textsubscript{3}\textsuperscript{-} can be estimated by assessing the concentration of preformed NO\textsubscript{3}\textsuperscript{-} at the Southern Ocean surface where a particular isopycnal was ventilated. The δ\textsuperscript{15}N of the remineralised component can be calculated by using Rayleigh systematics as shown in equations (1.2), (1.3) and (1.4). Here I calculate the predicted δ\textsuperscript{15}N of remineralised NO\textsubscript{3}\textsuperscript{-} assuming closed system dynamics. As the preformed NO\textsubscript{3}\textsuperscript{-} at the surface decreases further north, the remineralised product becomes heavier as more δ\textsuperscript{15}N is consumed by phytoplankton. The Δ(15-18) of the remineralised product can then be calculated using an estimation for δ\textsuperscript{18}O\textsubscript{rem} of 1.1‰ (Sigman et al., 2009b). The Δ(15-18)\textsubscript{rem} therefore increases further north into
the subantarctic as the preformed NO$_3^-$ at the surface is consumed. From this reasoning I can estimate Δ(15-18)$_{\text{remin}}$ and the Δ(15-18) at each isopycnal or depth. Assuming that the Δ(15-18) of preformed NO$_3^-$ is 3.5‰ (UCDW values - see Chapter 4 ), the proportion of Δ(15-18)$_{\text{remin}}$ and Δ(15-18)$_{\text{preformed}}$ can then be used to calculate the Δ(15-18)$_{\text{total}}$. The lowest Δ(15-18) calculated from this process is ~2.5‰, between 300-500 m (Figure 3.9). The low Δ(15-18) identified in our transect is much shallower and lower in value in the transect and therefore does not appear to be a result of preferential consumption of $^{14}$N in the Southern Ocean surface. This directs our attention to other mechanisms that could cause this lower Δ(15-18) at shallower depths in the SASW.

Redox processes have been inferred as drivers for a decoupling of N and O, leading to lower Δ(15-18) in other regions of the ocean (Sigman et al., 2005), however in this transect the water column is well oxygenated arguing against any reduction of NO$_3^-$ via this process. A source of low $\delta^{15}$N$_{\text{NO3}}$, may result from the preferential release of $^{14}$N from sinking particles. If this were the case there would be an observed increase $\delta^{15}$N of particulate N with the observed decrease in Δ(15-18). Instead of this, there is a similar trend in $\delta^{15}$N$_{\text{PN}}$, where the lowest values across the transect are observed at ~100 m. Below this, $\delta^{15}$N$_{\text{PN}}$ increases which may cause a slightly lower Δ(15-18) at greater depths (although negligible because of low concentrations). However this mechanism would not explain the low Δ(15-18) between 100-200 m over most of the transect. Indeed, previous studies have observed an increase in sinking N $\delta^{15}$N with depth is normally observed (Voss et al., 1996; Altabet and Francois, 2001; Thunell et al., 2004). The discrimination of N isotopes during NH$_4^+$ oxidation has a high isotopic effect of ~14-30‰ (Casciotti et al., 2003), but would not have an isotopic effect on $\delta^{15}$N$_{\text{NO3}}$ unless there is either an accumulation of NH$_4^+$ or a significant loss term. NH$_4^+$ accumulation only occurs in regions where N is not limiting and it is therefore produced faster than it is consumed. In the SASW there is an accumulation of NH$_4^+$ at the base of the mixed layer likely a result of iron limitation leading to incomplete N utilisation (Browning et al., 2014).
Figure 3.9 Modelling the effects of NO$_3^-$ remineralisation on $\Delta$(15-18) in the Subantarctic Zone (SAZ). a. The change in isotopic fractionation as nitrate is progressively consumed in the SAZ and its effect on the preformed and remineralised nitrate. The isopycnals 27, 26.8, 26.4 and 26.2 are identified in comparison to the nitrate concentrations at which they ventilate. b. The $\Delta$(15-18) measured is compared to the modelled $\Delta$(15-18) using the approach used in a. The lightest measured values are found at lighter isopycnals compared to the modelled values, suggesting other processes are causing lighter $\Delta$(15-18) between 100-200 m.

Using the concentrations of NH$_4^+$ and NO$_3^-$, the proportion of NH$_4^+$ that comprises the fixed N pool can be calculated. In the SASW, NH$_4^+$ concentrations constitute up to 10% of the available fixed N (Figure 3.10). Using Equations 1.2 and 1.4, and an isotope effect of 15‰, I can calculate the effect that a residual pool of NH$_4^+$ would have on the surrounding NO$_3^-$ isotope characteristics as $^{14}$N is preferentially oxidized. If I assume an initial value of 6‰ for NO$_3^-$, this would leave the residual remineralised $\delta^{15}$N$_{NO_3}$ at 1.5‰. If I assume that $\delta^{18}$O$_{NO_3remin}$ is 1.1‰, this would lead to a $\Delta$(15-18) of 0.4‰. Therefore this mechanism seems to describe the dynamics of the SASW. The decoupling between the two isotope systems correlates well with
high proportions of NH$_4^+$. Although the low $\Delta$(15-18) identified south of the front may result from the build-up of NH$_4^+$ that is visible in our profiles, NH$_4^+$ is absent from the subtropical waters requiring another mechanism to be driving this low $\Delta$(15-18).

![Figure 3.10](image)

**Figure 3.10** The proportion of dissolved fixed N pool that is sourced from NH$_4^+$ compared to NO$_3^-$ (plus NO$_2^-$) is displayed with colours, red denoting up to 10%. Overlaid contours show the $\Delta$(15-18) signatures across the transect, with areas in the SASW with high NH$_4^+$ correlating with low $\Delta$(15-18).

In most regions of the ocean NH$_4^+$ is difficult to determine separately from organic matter as it is consumed very rapidly by phytoplankton. NH$_4^+$ is easier to photosynthesise than NO$_3^-$, therefore is preferentially consumed. The build-up of NH$_4^+$ therefore suggests that it is not being actively consumed by phytoplankton in this region. A recent study found the SASW to be Fe limited (Browning et al., 2014). As there is a large amount of fixed N available, and limiting Fe concentrations, the rapid consumption of NH$_4^+$ is not necessary, as biological demand for N is low. The subantarctic is principally Fe limited, therefore this may support the presence of NH$_4^+$ in much of the surface waters across this region. Blooms of diatoms developing in late spring are common in the subantarctic, which decrease silicate (Si) over the productive season. Any available Fe is rapidly consumed and produces diatoms that are heavily silicified leading to a high depletion of Si in relation to N (De La Rocha et al., 2000). This is demonstrated in the negative Si* values in the
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SAMW which form in these regions (Sarmiento et al., 2004). A recent study in the Atlantic sector of the subantarctic found high NH$_4^+$ concentrations corresponding with these regions (Le Moigne et al., 2013). These high NH$_4^+$ concentrations correspond with post diatom bloom areas where Si:N ratios are low and biological uptake of N decreases from the limitation by Fe and Si. In this work I find evidence for low Δ(15-18) signatures in subantarctic waters caused by residual NH$_4^+$ concentrations. NH$_4^+$ is normally quickly consumed by biota, therefore the fractionation by NH$_4^+$ oxidation is not usually expressed. High concentrations of NH$_4^+$ further support low biological demand for N, and provide the opportunity for nitrification to express a lighter N signature on the nitrate pool of the SASW.

### 3.5.3.2 Contribution from new N sources to export production

The subantarctic regions of the transect have high preformed concentrations of fixed N and low biological demand for N, as Fe is limiting production (Browning et al., 2014). For these reasons, I focus on quantifying the sources of N to the subtropical regions of the transect, where fixed N is limiting production, and fluxes are likely to have a direct impact on primary production. As I am able to rule out all of the above mechanisms in adding low Δ(15-18) in the subtropical water masses, the remaining processes to lower the amount of δ$^{15}$N$_{NO_3}$ are the addition of fixed N via N$_2$ fixation or atmospheric deposition. As new N is added to water masses it leaves a low $^{15}$N signature on NO$_3^-$ that is remineralised and recycled in subtropical waters. The isotopic signature of NO$_3^-$ therefore is an integrated representation of different sources of NO$_3^-$ to the water mass. Previous studies of NO$_3^-$ isotopes in subtropical regions have found low Δ(15-18) signatures, which have often been attributed to the addition of a low $^{15}$N source of fixed N to the surface ocean (e.g. Liu et al., 1996). Low Δ(15-18) has been identified in the North Atlantic, close to the Azores Front and in the Western Subtropical North Atlantic which are attributed to N$_2$ fixation (Knapp et al., 2008, Bourbonnais et al., 2009). The δ$^{15}$N of organic matter sourced from N$_2$ fixation has been measured between -2 and 0‰. As the organic matter of N$_2$ fixers is remineralised and converted back into NO$_3^-$, the N atoms retain this isotopic signature. Assuming O molecules are derived in some proportion from water and dissolved O$_2$ then δ$^{18}$O in newly remineralised NO$_3^-$ should be ~1.1% (Sigman et al.,
Tuerena, 2015

2009), and NO₃⁻ sourced solely from N₂ fixation would retain a Δ(15-18) of ~2.1‰. Therefore a contribution of fixed N from the process of N₂ fixation may be the cause of low Δ(15-18) in the subtropical thermocline.

The isotopic composition of fixed N deposited from the atmosphere has been found to be variable but averaging at low values, comparable to newly fixed N (Hastings et al., 2003; Knapp et al., 2010; Morin et al., 2009). As such there are inherent problems with separating out the inputs of atmospherically deposited N from newly fixed N. A meridional transect of the Atlantic found atmospheric derived NO₃⁻ between 40°S and 30°N to be ~4 ± 2‰ for natural sources and -0.5 to 5.9‰ for NO₃⁻ in air masses influenced by continental pollution. Total fixed N deposition close to Bermuda has been measured at ~2.3‰ (Knapp et al., 2010), and similar studies from the Sargasso Sea found values ranging from -6.2 to -2.1‰ over the course of warm and cool seasons (Hastings et al., 2003; Gobel et al., 2013). Anthropogenic inputs of fixed N to the ocean are increasing, with estimates of an increase from 5.8-53.6 Tg N yr⁻¹ from 1860-2000, and as such the percentage of total fixed N that is anthropogenically derived has increased from 29 to 80% (Duce et al., 2008). If I assume a median of the anthropogenic derived δ¹⁵N of Morin et al. (2009) of 2.8‰, then the isotopic input in 1860 would be ~2.0‰ and in 2000 ~1.4‰. Throughout this work I use a value of -2‰ as a conservative estimate although there remains a large degree of uncertainty around this number. This reinforces the need for a method of separating newly fixed and atmospherically derived N in stable isotope studies.

Both wet and dry atmospheric deposition have relatively high N:P ratios and low δ¹⁵N_NO₃ similar to N₂ fixation, making it difficult to separate out and quantify the two processes (Knapp et al., 2008). Atmospheric δ¹⁸O_NO₃ has much higher values of ~50-70‰ compared to δ¹⁵N_NO₃ (Morin et al., 2009), and therefore could significantly contribute to the Δ(15-18) with even a minuscule contribution. In this transect Δ(15-18) is not observed lower than ~0‰, therefore it is unlikely that there is any significant contribution of new atmospheric NO₃⁻ that has not been actively recycled, therefore resetting δ¹⁸O to ~1.1‰. If this atmospheric derived NO₃⁻ is added to the surface of a water mass and is rapidly consumed by phytoplankton, the process of
assimilation and remineralisation will reset $\delta^{18}O_{NO_3}$ to $\sim$1.1‰ yet the $\delta^{15}N$ would be retained. Atmospheric deposition therefore may lead to a decrease in the $\delta^{15}N_{NO_3}$ without significantly changing $\delta^{18}O$ towards an atmospheric signature. I can therefore estimate that fixed N sourced from atmospheric deposition would have a $\delta^{18}O_{NO_3}$ of $\sim$1.1‰ and $\delta^{15}N_{NO_3}$ of $\approx$-2‰. To estimate the flux of new N added via the process of atmospheric deposition, I use estimates from the literature. Baker et al. (2010) estimate fluxes of 8.5 mmol N m$^{-2}$ yr$^{-1}$ on the western boundary of the South Atlantic and 1.9 mmol N m$^{-2}$ yr$^{-1}$ on the central and eastern areas of the transect. Using these estimates I can investigate the influence that they may have on the observed light $^{15}N$ signatures in the subtropical water masses.

Above I have identified the two possible causes for the low $\delta^{15}N$ signatures in the subtropical water masses at 40°S. Using estimates of $\delta^{15}N$ fluxes via atmospheric deposition, the flux of newly fixed N via diazotrophs that is driving export production can be calculated. The construction of an isotope mass balance model can be used to quantify the relative sources of low $\Delta(15-18)$ in the subtropical waters. I first approach this by identifying the extent of export production that has been supplied by a lower $\delta^{15}N$ than the subsurface source. As fixed N within the mixed layer is a limiting nutrient in these regions, the magnitude and $\delta^{15}N$ of PN exported from the surface layer should be balanced by the supply of $\delta^{15}N$ from the subsurface, atmospheric deposition and N$_2$ fixation. The export of PN is quantified by using our estimates of the $\delta^{15}N$ of particulate matter at 100 m combined with $^{234}$Th derived fluxes of particle export out of the surface layer, which provides us with a flux of $\delta^{15}N$ export. The supply from the subsurface is quantified by using the concentrations and isotopic ratios of NO$_3^-$ from 200 m, as the base of the winter mixed layer (Equations 3.6 and 3.7). With this approach the export flux of $\delta^{15}N$ from the surface layer can be assessed to identify whether there is a significant supply of N that is required from a low $\delta^{15}N$ source to drive the PN to lower $\delta^{15}N$ (Figure 3.11). The flux of N from N$_2$ fixation driving particle export can be estimated by calculating the proportion of NO$_3^-$ required from a source of -1‰ to balance export and supply. To further address the potential for atmospheric deposition to be contributing low $\delta^{15}N$, I then calculate the maximum contribution from atmospheric
deposition using concentration estimates (Baker et al., 2010). This is calculated using \( \delta^{15}\text{N}_{AD} = -2\%o \) and the maximum \( \delta^{15}\text{N}_{AD} \) flux is subtracted from the N\(_2\) fixation estimate to calculate the extent to which atmospheric deposition would overestimate the effects of N\(_2\) fixation (Table 3.1).

\[
\begin{align*}
(N_{200\ m} - N_{100\ m}) \times K_u + F_{\text{fix}} + F_{\text{AD}} &= F_{\text{PN}} \\
((\delta^{15}\text{N}_{200\ m} \times N_{200\ m}) - (\delta^{15}\text{N}_{100\ m} \times N_{100\ m})) \times K_u + \delta^{15}\text{N}_{\text{fix}} \times F_{\text{fix}} &+ F_{\text{fix}} + F_{\text{AD}} = \delta^{15}\text{N}_{\text{PN}} \times F_{\text{PN}}
\end{align*}
\]

\( N_{100\ m} = \text{NO}_3^- \text{ at 100 m, } N_{200\ m} = \text{NO}_3^- \text{ at 200 m, } K_u = \text{vertical exchange between surface and subsurface waters, } F_{\text{fix}} = \text{fraction from N}_2 \text{ fixation, } F_{\text{AD}} = \text{fraction from atmospheric deposition, } F_{\text{PN}} = \text{flux of PN export, } \delta^{15}\text{N}_{\text{fix}} = \delta^{15}\text{N} \text{ of newly fixed material, } \delta^{15}\text{N}_{200\ m} = \delta^{15}\text{N}_{\text{NO}_3} \text{ at 100 m, } \delta^{15}\text{N}_{100\ m} = \delta^{15}\text{N}_{\text{NO}_3} \text{ at 100 m.}
Table 3.1 Export production estimates from $^{234}$Th measurements are shown for each Station within the subtropical water masses across the 40°S transect. Column 3 displays the total export production using $^{234}$Th measurements. Columns 4-6 show model output of the proportion of export production which is supported by subsurface nitrate (SS), atmospheric deposition (AD) and N$_2$ fixation (NF). Estimates are calculated using Equations 3.6 and 3.7. The final column shows the estimate of the flux of export production supplied by newly fixed N, in mmol N m$^{-2}$ d$^{-1}$.

<table>
<thead>
<tr>
<th>Water mass</th>
<th>Station</th>
<th>Export production mmol N m$^{-2}$ d$^{-1}$</th>
<th>f SS</th>
<th>f AD</th>
<th>f NF</th>
<th>Newly fixed N mmol N m$^{-2}$ d$^{-1}$</th>
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<td>0.01</td>
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<tr>
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</tr>
<tr>
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<td>0.15</td>
<td>0.09</td>
<td>0.77</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Estimates of atmospheric deposition fluxes across the transect fall between 5-27 x10$^{-3}$ mmol N m$^{-2}$ d$^{-1}$, significantly lower than calculated N$_2$ fixation fluxes (Table 3.1). Our estimates of atmospheric deposition are larger on the western boundary (up to 0.027 mmol N m$^{-2}$ d$^{-1}$) compared to the eastern boundary (up to 5-7 x10$^{-3}$ mmol N m$^{-2}$ d$^{-1}$) and thus have larger effects on our N$_2$ fixation estimates. On the western boundary, the Brazil Current flows down the east coast of South America and thus the effects of atmospheric deposition are likely to be higher from the large cities located in this region. Even so, the amount of fixed N that is supplied via diazotrophs appears to be much higher than the effects of atmospheric deposition (Table 3.1). The lower $\delta^{15}$N of atmospheric deposition (-2‰) compared to organic matter sourced from N$_2$ fixers does not appear to have a large effect on our estimates. The extent at which atmospheric deposition fuels export production ranges from 1 to 9% across the transect (Table 3.1). Figure 3.12 also illustrates the influence of atmospheric N on export production, with the highest estimates on the western boundary compared to lower estimates in the Agulhas Current and the SACW. These estimates can account...
for up to 12 mmol N m\(^{-2}\) yr\(^{-1}\) of exported nitrogen on the western boundary of the transect.

### 3.5.3.3 N\(_2\) fixation in subtropical Atlantic

N\(_2\) fixation fuels a significant proportion of export production in the subtropical water masses at 40°S (Figure 3.12, Table 3.1). It has long been recognised that there is a significant flux of newly fixed N to the subtropical North Atlantic, with estimates between 20-35 Tg N yr\(^{-1}\) (Deutsch et al., 2007; Hansell et al., 2007; Yoshikawa et al., 2013, Chapter 4) What has not been investigated before is the extent by which this fixed N fuels productivity within the whole subtropical Atlantic basin. There remains a paucity of estimations of the importance of N\(_2\) fixation to productivity rates in the South Atlantic, with most previous studies concentrating on the North Atlantic. Deutsch et al. (2007) estimate that approximately 50% of particulate N derived from the subtropical gyre is of N\(_2\) fixation origin, making it the principal supply of fixed N in the low latitude ocean. Indeed this has been suggested by isotopic studies in many regions of the low latitude ocean (Liu et al., 1996; Knapp et al., 2008; Casciotti et al., 2008; Bourbonnais et al., 2009) and therefore could be interpreted as N\(_2\) fixation occurring at rates that are sufficient to cause an accumulation of lighter N in the subtropical basins. Here N\(_2\) fixation supports ~1/3 of export production and up to ~3/4 in the Brazil Current, suggesting the accumulation of fixed N within subtropical water masses. To our knowledge, this is the first study using the stable isotopes of NO\(_3^-\) to estimate the rates of productivity fuelled from N\(_2\) fixation in the South Atlantic surface waters. The estimates are ~50% of the export rates estimated from the NE Atlantic (Bourbonnais et al., 2009) and range between 20-120 mmol N m\(^{-2}\) yr\(^{-1}\) compared to the NE Atlantic rates of 56-269 mmol N m\(^{-2}\) yr\(^{-1}\). This study was carried out in austral summer; therefore our estimates here provide a high end estimate of the N\(_2\) fixation supply to productivity rates in the South Atlantic. It does however highlight the importance of N\(_2\) fixation to supplying the subtropical surface waters with fixed N even as far south as the SSTC. This study suggests that fixed N is added and actively recycled within the sub-tropical water masses on its transit to the SSTC, supplying a significant proportion of N to the export flux from the surface layer.
In the SACW located at the centre of the transect there is evidence of N$_2$-fixed N fuelling export production, though to a lesser extent than on the western margin of the transect within the Brazil Current. The core of the SACW has been eroded by the high degree of mixing with subantarctic waters which accounts for the higher proportion of subsurface NO$_3^-$ supplying productivity and export. In contrast, within the Brazil Current N$_2$ fixation can account for up to ~75% of the fixed N fuelling primary productivity (Figure 3.12), which are the highest estimates within the transect. *Trichodesmium* abundance has been found to be very low or absent between 5 and 30$^\circ$S, which argues against fixed N being added within the South Atlantic (Tyrrell et al., 2003). However recent work suggests that there may be a presence of unicellular diazotrophs which are harder to identify and may have been overlooked in previous work (Moore et al., 2014). This light signature may result from exchange within the North Atlantic basin and be carried in the Brazil Current from its formation in equatorial regions. However since fixed N would be increasingly lost from the surface via export production to sustain a light signature from diazotrophs it is likely that a proportion of this signal is from in situ N$_2$ fixation within the South Atlantic basin. The large contribution of newly fixed N therefore supports recent evidence that N$_2$ fixers may be significant on the western boundary of the South Atlantic. This highlights the effectiveness of isotopic tracers at identifying signals irrespective of the diazotroph species present.
At the core of the Agulhas leakage identified within our transect, ~1/3 of production is sourced from N$_2$ fixation and up to 0.2 mmol N m$^{-2}$ d$^{-1}$, approximately 2/3 of the flux sustained within the Brazil Current (Table 3.1). These waters are sourced from the Indian Ocean and lighter N must either be produced in situ or transported within the Agulhas Current from the Indian Ocean. In the subtropical surface water masses NO$_3^-$ concentrations are very low within the mixed layer and have been found to be limiting productivity (Browning et al., 2014). It is therefore not surprising that a significant proportion of the fixed N that is fuelling productivity may be sourced N$_2$ fixation. These light signatures indicative of N$_2$ fixation may be transferred within subtropical water masses from the North Atlantic, or there may be significant inputs of newly fixed N from the subtropical Indian Ocean or the South West Atlantic. In the next section I explore the isotopic ratios within NO$_3^-$ in these regions to try to identify the areas where N$_2$ fixation is significantly adding fixed N to the subtropical thermocline. This is important for our understanding of the spatial variability of new
N additions, which may help to disentangle the factors which limit diazotroph abundance within the subtropical ocean.

### 3.5.4 A wider view of Atlantic N cycling

As an increasing amount of NO$_3^-$ isotope data is emerging from the literature, the observed values can be used to establish a wider view of how isotope signatures evolve in the subtropical thermocline. A well categorised transect at 40°S in the Atlantic gives end member values of subtropical gyre waters at their furthest movement south. Within this transect the SACW and Brazil Current can be compared to a dataset of NO$_3^-$ isotopes from the North Atlantic (Knapp et al., 2008) and the Agulhas leakage compared to data from the subtropical Indian Ocean (U. Tsunogai, Intermediate Data Product). Changes along isopycnal gradients can help to decipher the main areas where newly fixed N is sourced.

#### 3.5.4.1 Atlantic Basin

The North Atlantic thermocline has been studied extensively for its role in adding newly fixed N to the thermocline. High N:P ratios associated with *Trichodesmium* blooms have long been observed in the North Atlantic in comparison to the South Atlantic gyre, fuelled by high Fe concentrations (Moore et al., 2009). The addition of newly fixed NO$_3^-$ has also been observed in the North Atlantic thermocline from the use of NO$_3^-$ isotopes, both in the Sargasso Sea and the Azores Front (Knapp et al., 2008; Bourbonnais et al., 2009). It has been considered that these low δ$^{15}$N signatures represent a basin wide signal, as models estimate a high degree of exchange between the north and south (Knapp et al., 2008). This suggests that circulation homogenises the δ$^{15}$N signal of newly fixed N within the thermocline. They found that if N$_2$ fixation were occurring only in the North Atlantic, ~37 % of recently fixed N would accumulate in the South Atlantic, suggesting 7 % more transport northward than southward (Knapp et al., 2008). This therefore leads to a slight tendency for recently fixed N to accumulate in the Sargasso Sea thermocline compared to the South Atlantic. Our estimates from the Brazil Current suggest additional fixed N produced in the South West Atlantic is important to sustain a high contribution of recently fixed N.
Figure 3.13 A comparison of $\delta^{15}N$ and N* of the subtropical water masses at 40°S with the subtropical North Atlantic and Indian Oceans. The $\delta^{15}N$ and N* of the Atlantic and Indian SAMW is highlighted with black diamonds, and from these points the expected projection of $\delta^{15}N$ and N* with low and high nitrate waters is shown. The coloured dashed lines indicate how the addition and loss of nitrate from N fixation would change N* and $\delta^{15}N$, depending on the concentration of the water mass (as defined in the legend). Subtropical data from the North Atlantic (Knapp et al., 2008) is distinct from the Indian Ocean (U. Tsunogai, IDP).

In Figure 3.13, these ideas are considered, as $\delta^{15}N_{NO_3}$ is plotted against N* concentrations. Compared to the South Atlantic SAMW, the North Atlantic data (taken from Knapp et al., 2008), fall on a trend of decreasing $\delta^{15}N_{NO_3}$ with increasing N* concentration (as discussed in Chapter 4). Where nitrate concentrations are lower (closer to the surface), lower $\delta^{15}N$ is observed per given N* concentration, as it contributes a higher proportion of the total nitrate. The SACW has much lower N* concentrations and higher $\delta^{15}N_{NO_3}$ compared to the North Atlantic. The SACW forms close to the Brazil Malvinas Confluence Zone (BMC), where it moves east as the southern limb of the South Atlantic gyre. The $\delta^{15}N_{NO_3}$ of these waters is higher than the North Atlantic equivalent, as any signal of newly fixed N would be overpowered by the influence of subsurface nitrate. In contrast, the Brazil Current which moves south along the western boundary has communicated with the South
Equatorial Current. This may provide reasoning for the lower $\delta^{15}$N identified in this water mass. Comparing these two subtropical water masses shows that the older, more saline waters of the Brazil current have a lower $\delta^{15}$N than the younger SACW, which may demonstrate that a higher amount of exchange has occurred in these waters (Knapp et al., 2008). However if the low $\delta^{15}$N were solely from the North Atlantic, the Brazil Current would progressively lose nitrate as a proportion is exported from the surface layer in transport. Any resupply from the thermocline in contrast would likely have an isotopic signature close to the SAMW (in the Southern basin). In conclusion, low $\delta^{15}$N$_{NO3}$ and $\delta^{15}$N$_{PN}$ in the South Brazil Current is likely supplied in part by in situ $N_2$ fixers within the South West Atlantic.

3.5.4.2 Agulhas Leakage

The Agulhas Current forms from the Indian Subtropical gyre. These waters move southwards from Madagascar, around the coast of Africa before moving into the Atlantic Ocean. The $\delta^{15}$N$_{NO3}$ of the Indian SAMW and the subtropical gyre are higher than the Atlantic, likely from the influence of water column denitrification within the Indian basin. From the Indian SAMW to the Agulhas current, $\delta^{15}$N$_{NO3}$ decreases and $N^*$ increases indicating that a source of lighter N is added along its transit. This change towards lighter $\delta^{15}$N within the Agulhas retroflection supporting the hypothesis that light $\delta^{15}$N is being added by diazotrophs within the western boundary current. The role of diazotrophs within the Indian Ocean is still relatively unexplored. Considering the abundance of Fe and P within this basin, it is likely that $N_2$ fixers play a vital role in supplying fixed N to the global ocean.

Both the Agulhas Current and the Brazil Current have high Fe:N ratio and P:N ratios as described in Ward et al. (2013), further supporting these observations that the two subtropical western boundary currents of the South Atlantic and Indian Ocean are likely to be important regions for diazotroph success. These regions have been relatively understudied in the past. The use of isotopic tracers can help to fill this gap and further work is needed to underpin the relative importance of these two regions on a global scale.
3.6 Conclusions

A thorough examination of the stable isotope cycling of particulate and dissolved N across the South Atlantic subtropical front has elucidated the processes which cycle fixed N in this region. Two contrasting regimes are identified north and south of the front with different N cycling processes affecting primary productivity. Subantarctic waters have high NO$_3^-$ concentrations and measureable fractionation of NO$_3^-$ by algal consumption. Here, remineralisation and resupply do not appear to have a significant effect on productivity. In subtropical waters remineralisation provides the dominant supply of nutrients to phytoplankton and a significant proportion of this is from newly fixed N. To the south of the SSTC, in NO$_3^-$ replete conditions, mixing dilutes the thermocline NO$_3^-$ and an isotopic effect of ~5‰ is observed from 200 m to the mixed layer. Mixing dilutes the fractionation of N and O in thermocline waters across all salinities, but decoupling of N and O isotopes away from consumption processes highlights the importance of recycling processes.

Low Δ(15-18) is observed in the subantarctic and subtropical thermocline, lower values in the subtropical waters suggest different mechanisms. Observed high NH$_4^+$ concentrations may explain low Δ(15-18) in the SASW. Residual NH$_4^+$ would retain $^{15}$N thus resulting in remineralised NO$_3^-$ with a lower $^{15}$N. Thus in an Fe limited environment, low biological N demand and recycling efficiency may lead to low Δ(15-18) production. In subtropical water masses, a source of light δ$^{15}$N$_{NO_3}$, either from N$_2$ fixation or atmospheric deposition, is required to explain this low Δ(15-18) in the subtropical thermocline. Approximately 1/3 of export production in the subtropical water masses is from newly fixed N, this estimate increases to ~75% in the core of the Brazil Current. N$_2$ fixation derived export rates are higher than our upper estimates of atmospheric deposition for all of the stations. This study suggests that although N$_2$ fixers are not evident across this region, the fixed N added by diazotrophs in water mass transport, is significant at fuelling productivity in this region. The low δ$^{15}$N$_{NO_3}$ and δ$^{15}$N$_{PN}$ in the Brazil Current further suggest that N$_2$ fixation may add new N in the subtropical western boundary current.
4 Nutrient cycling in the Atlantic basin: the evolution of nitrate isotope signatures in water masses

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R.E. Tuerena¹, R.S. Ganeshram¹, W Geibert¹, A. E. Fallick², J. Dougans², A. Tait², S.F. Henley³ and E.M.S. Woodward⁴

Affiliations:

¹Grant Institute, University of Edinburgh, Edinburgh, UK.

²Scottish Universities Environmental Research Centre, Rankine Avenue, East Kilbride, Scotland, UK.

³Plymouth Marine Laboratory, Plymouth, UK.

Contributions:


R.E. Tuerena: Sample analysis.

E. Malcolm S. Woodward: Nutrient analysis at sea.

R.E. Tuerena: Initial paper draft.

R.E. Tuerena, R.S. Ganeshram: Discussion of results and subsequent editing of drafts.
4.1 Abstract

A basin-wide transect of nitrate isotopes ($\delta^{15}N_{NO_3}$, $\delta^{18}O_{NO_3}$) in deep water masses across 40°S in the South Atlantic is used to investigate Atlantic nutrient cycling and the communication pathways of nitrogen cycling processes. Intermediate waters formed in the subantarctic are enriched in $\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$ from partial utilisation by phytoplankton and distal denitrification processes, transporting enriched signatures to the subtropical Atlantic. Water mass modification through the Atlantic is investigated by comparing data from 40°S and 30°N. This reveals nitrate in the upper intermediate waters is recycled as it transits through the subtropical Atlantic, as evidenced by decreases in $\delta^{18}O_{NO_3}$. We document diazotrophy producing high N:P particles (18-22) for remineralisation which is further confirmed by a decrease in $\delta^{15}N_{NO_3}$ through the subtropical Atlantic. Modification of $\delta^{15}N_{NO_3}$ signatures through the Atlantic thermocline are used to estimate basin-scale N$_2$ fixation of ~26-36 Tg N yr$^{-1}$. The rate of N$_2$ fixation calculated is higher than current estimates of excess phosphate supplied to the Atlantic basin, the mechanisms which may cause this discrepancy are discussed. This study records heavy isotopic composition of Southern Ocean sourced intermediate waters and their subsequent transformation to lighter $\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$ as they flow under the Atlantic thermocline. These modifications influence the isotopic signatures on North Atlantic Deep Water (NADW) which is subsequently exported from the Atlantic. This work reveals the dominance of recycling processes and diazotrophy on nitrate cycling in the Atlantic. These processes provide a source of low $\delta^{15}N_{NO_3}$ to the Southern Ocean via the NADW, to counteract enrichments in $\delta^{15}N_{NO_3}$ from water column denitrification in the Indo/Pacific basins. Therefore, the balancing the Atlantic N budget and isotopic signatures require timescales of oceanic mixing.
4.2 Introduction
Nitrate (NO$_3^-$) is an essential nutrient for marine phytoplankton and limits primary production in much of the global ocean. Nitrate supply to the surface ocean therefore has implications on the efficiency of the biological pump and CO$_2$ regulation. Denitrification and nitrogen (N$_2$) fixation by diazotrophs are the main source and sink of NO$_3^-$ in the ocean and hence exert a predominant control on the ocean NO$_3^-$ inventory and mass balance (Gruber, 2004). Nevertheless, these processes are spatially separated in the ocean. Water column denitrification at globally significant rates, occur in the northern Indian and eastern Pacific Ocean basins. N$_2$ fixation may occur spread over the tropics and subtropics determined by the availability of excess P and Fe (Deutsch et al., 2007; Moore et al., 2009). N loss from the ocean and thus a P build-up in excess of Redfield nutrient stoichiometry (16N:1P), may encourage the growth of N$_2$ fixers and provide a negative feedback within the N cycle (Deutsch et al., 2007). Such feedback is crucial in controlling the marine N inventory which has a turnover time of ~3000 years (Deutsch et al., 2004). Whether these two processes are balanced within each basin may determine how quickly the marine N cycle can respond to perturbations (Weber and Deutsch, 2014). Isotopic studies of NO$_3^-$ in the ocean can clarify this and identify the water mass pathways through which the processes of N loss and gain communicate.

In the Atlantic, the northward flow of intermediate and bottom waters feed the formation of the North Atlantic Deep Water (NADW), which ventilates the global ocean. The NADW provides approximately half of the deep waters of the global ocean and has higher N:P concentrations compared to Southern Ocean deep waters (Moore et al., 2009). These differences may be attributed to the spatial segregation between denitrification and N$_2$ fixation in the ocean (Moore et al., 2009). The Atlantic Ocean is thought to be where N$_2$ fixation exceeds denitrification, a result of negligible N loss from the Atlantic water column. Thus NO$_3^-$ isotopic properties of water masses in the Atlantic can further clarify the water mass pathways through which these signatures are transported in the Atlantic basin and through the global ocean.
Stable NO$_3^-$ isotopic signatures are integrative tracers which can provide information on the efficiency of N recycling processes as well as the sources and sinks of N in the ocean. The $^{15/14}$N and $^{18/16}$O of NO$_3^-$ are sensitive to biogeochemical cycling and can provide information about the origin and transport of water masses (Sigman et al., 2000). Nitrogen and oxygen isotope signatures in NO$_3^-$ ($\delta^{15}$N$_{NO3}$ and $\delta^{18}$O$_{NO3}$) can be used as tracers of N cycling processes which may vary temporally and spatially within the ocean (DiFiore et al., 2006, Rafter et al., 2013). Isotope ratios are measured relative to a reference (AIR, VSMOW) and are expressed as a delta notation ($\delta^{15}$N vs AIR (‰) = ($R_{\text{sam}}/R_{\text{std}}$ - 1) x 1000 and $\delta^{18}$O vs VSMOW (‰) = ($R_{\text{sam}}/R_{\text{std}}$ - 1) x 1000). The isotopic effect (defined here in per mil notation as $\varepsilon=\frac{15}{14}K - 1$, where $^{14}$K and $^{15}$K are the rate coefficients of $^{14}$N and $^{15}$N) of N cycling processes, may leave an isotopic “fingerprint” on NO$_3^-$ within water masses. This can provide information on the processes that occurred in water mass formation and the subsequent modification during transport from nutrient remineralization and physical mixing processes (DiFiore et al., 2006, Rafter et al., 2013). The integrated nature of these isotopic signatures helps to avoid the complexities in upscaling shipboard measurements of spatially and temporally variable N cycling processes and assumptions in modelling estimates (Sigman et al., 2009).

The average subsurface oceanic $\delta^{15}$N$_{NO3}$ is close to 5‰ and, globally, can be interpreted as a balance between isotopic fractionation of N$_2$ fixation and denitrification (Sigman et al., 2009). Nitrate consumption by phytoplankton acts to enrich the residual pool of NO$_3^-$ in $^{15}$N, with an isotopic effect of $\sim$5‰ (Altabet and Francois, 2001). However, in most surface waters, NO$_3^-$ is fully consumed by phytoplankton. In these regions uptake and remineralization is thought to have little effect on subsurface $\delta^{15}$N$_{NO3}$, as remineralized organic N should be similar to the source NO$_3^-$ (Sigman et al., 2000). In the Southern Ocean, however, NO$_3^-$ concentrations remain high, a result of low light levels and iron limitation during photosynthesis (e.g. Boyd et al., 2007). Partial utilization of nutrients leaves an isotopic imprint on preformed nutrients in intermediate waters formed in the Southern Ocean, of higher $^{15}$N and $^{18}$O with decreasing NO$_3^-$ (Sigman et al., 2000).
The deviations away from the isotopic effect of NO$_3^-$ utilization ($5\%$) can be used to indicate both physical and biogeochemical changes during water mass formation.

As isotopic fractionation by NO$_3^-$ consumption does not impact subsurface NO$_3^-$ in most regions of the ocean, deviations in subsurface $\delta^{15}$N$_{NO3}$ can be indicative of processes far beyond the localized regions of water mass formation or NO$_3^-$ input/output. Nitrate added to the ocean by N$_2$ fixation is not fractionated during atmospheric N$_2$ uptake therefore newly fixed N has light signatures ($\sim 1\%$) (Carpenter et al., 1997). This process adds NO$_3^-$ relatively depleted in $^{15}$N compared to mean subsurface NO$_3^-$. The isotope effect of water column denitrification is 20-30$\%$ (Brandes et al., 1998; Altabet et al., 1999; Sigman et al., 2003) and N loss during this process leaves an enriched imprint on $\delta^{15}$N$_{NO3}$.

The O isotopes of NO$_3^-$ are consumed with a similar isotopic effect to N ($^{15}e = ^{18}e$) for both algal consumption and denitrification during the process of NO$_3^-$ reduction (Granger et al., 2004, Karsh et al., 2012). It has been found in numerous studies that as denitrification or NO$_3^-$ utilization proceeds, $\delta^{15}$N$_{NO3}$ and $\delta^{18}$O$_{NO3}$ become increasingly enriched along a 1:1 trajectory (DiFiore et al., 2009; Sigman et al., 2009a). In contrast to NO$_3^-$ consumption, the production of NO$_3^-$ has different effects on $\delta^{15}$N$_{NO3}$ and $\delta^{18}$O$_{NO3}$. In the process of nitrification $\delta^{18}$O$_{NO3}$ is “reset”, with new NO$_3^-$ producing a signature of $\sim 1.1\%$ above the in situ $\delta^{18}$O of seawater (Sigman et al., 2009). $\delta^{18}$O$_{H2O}$ of seawater is relatively homogenous, with typical values for the global ocean between -0.4 to 0.5$\%$ (Bigg and Rohling, 2000). Given the small range of variability in $\delta^{18}$O of seawater, reflecting mainly salinity in the deep ocean, this process produces a relatively homogenous isotopic signature (Casciotti et al., 2002; Buchwald et al., 2012). The newly nitrified $\delta^{18}$O$_{NO3}$ therefore loses any previous enrichment from denitrification or partial utilization processes and is an absolute input of O atoms to NO$_3^-$. As nitrification is an absolute input of O, the difference between $\delta^{15}$N$_{NO3}$ and $\delta^{18}$O$_{NO3}$ can provide information on the importance of nitrification vs. utilization processes in the surface ocean (Sigman et al., 2005). As $\delta^{15}$N$_{NO3}$ is dependent on the fixed N pool at the time of nitrification, it captures isotopic signatures that $\delta^{18}$O$_{NO3}$ does not. This allows their coupled measurement to isolate the importance of processes such as NO$_3^-$ utilization, which fractionates both
isotopes equally, and nitrification processes, which affect $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ differently.

The difference in the processes that form NO$_3^-$ for N and O atoms has led to their dual measurement and the development of the parameter $\Delta(15\text{-}18)$ (defined here as $\delta^{15}\text{N}_{\text{NO}_3} - \delta^{18}\text{O}_{\text{NO}_3}$) (Rafter et al., 2013). This is increasingly used in NO$_3^-$ isotope studies to identify the different sources of remineralized NO$_3^-$ (Knapp et al., 2008). As both N and O isotopes are fractionated with the same isotopic effect for NO$_3^-$ consuming processes, a deviation away from a 1:1 relationship, and therefore shift in $\Delta(15\text{-}18)$, gives information about how NO$_3^-$ was formed. A low $\Delta(15\text{-}18)$ indicates the addition of low $^{15}\text{N}$ i.e. by remineralization of newly fixed organic matter ($\delta^{15}\text{N} = \sim -1\%_o$, $\delta^{18}\text{O} = \sim 1.1\%_o$) and a high $\Delta(15\text{-}18)$ can represent remineralization in NO$_3^-$ deplete areas ($\delta^{15}\text{N} = \sim 5\%_o$). This additional geochemical proxy for N cycling processes has been used in previous studies to estimate rates of N$_2$ fixation (Knapp et al., 2008), redox recycling processes (Sigman et al., 2005) and N regeneration over ocean basin scales (Rafter et al., 2013).

In this study, we present a full zonal transect of the $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ in the South Atlantic Ocean at 40°S (Figure 4.1). This allows the characterization of the basin-scale import of NO$_3^-$ through the Southern Ocean water masses and the export of NO$_3^-$ in the NADW. We use $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ data to disentangle the processes of their formation, modification during transport to understand the nutrient biogeochemistry of the Atlantic Ocean. This is compared with published data from the North Atlantic, and Indo-Pacific Basins. The formation of AABW and intermediate waters are investigated, and their characterization provides information on their modification in the Atlantic basin. Nutrient cycling in the subtropical Atlantic is investigated using $\delta^{18}\text{O}_{\text{NO}_3}$ and compared to estimates of nutrient remineralization from oxygen depletion. NO$_3^-$ isotope signatures of the NADW on export from the Atlantic basin is compared with deep water mass signatures of the Pacific and the Indian basins to understand the water mass pathways through which oceanic N loss and gain are linked through the global MOC.
4.3 Study area and Methods

Samples were collected onboard the RRS Discovery between October-November 2010 (D357) and the RRS James Cook between December 2011 and February 2012 (JC068) as part of the UKGEOTRACES 40°S transect. On both cruises, samples were collected on an east to west transect, with full water column sampling at each station. The transect captures collectively the Cape and Argentine basins of the South Atlantic, allowing full characterization of the water masses (Figure 4.1). The two cruise legs were intercalibrated with two repeat stations, which showed comparable nutrient concentrations and isotope abundances (within 1σ) below 500 m. Here, we examine the subsurface water masses; therefore seasonal variability should not affect our interpretations. Nitrate and nitrite concentrations (herein referred to as NO$_3$) were determined using an AA III segmented-flow Auto Analyser (Bran & Luebbe) following colorimetric procedures (Woodward and Rees, 2001.) Salinity, temperature and depth were measured using a CTD system (Seabird 911+) and salinity was calibrated on-board with discrete samples using an Autosal 8400B salinometer (Guildline). Dissolved O$_2$ was determined by a Seabird SBE 43 O$_2$ sensor and calibrated using a photometric automated Winkler titration system (Carritt and Carpenter, 1966).

Water samples for NO$_3$ isotope analysis were collected from the stainless steel rosette; seawater was filtered through an online Acropak filter (0.4 µm) into acid clean 60 ml Nalgene bottles and frozen at -20°C. Nitrate $\delta^{15}$N and $\delta^{18}$O were determined by the bacterial conversion of NO$_3$ to N$_2$O via the Denitrifier Method using denitrifier strain Pseudomonas aureofaciens (Sigman et al., 2001; Casciotti et al., 2002; McIlvin and Casciotti, 2011). Sample analysis was carried out at the Scottish Universities Environmental Research Centre (SUERC) and The University of Edinburgh following the GEOTRACES Science plan (http://www.geotraces.org/science/science-plan). Isotopic analysis was carried out at SUERC using a custom built GC-IRMS system in line with a VG Prism III isotope ratio mass spectrometer. Sample analysis at the University of Edinburgh used a Gasbench II coupled with a Delta Advantage +. On both instruments, isotopic measurements of sample N$_2$O were measured relative to a reference peak. Absolute
measurements of $\delta^{15}$N$_{NO3}$ and $\delta^{18}$O$_{NO3}$ were corrected to AIR and VSMOW respectively, with the use of international reference standards USGS32, USGS34 and USGS35. One blank and all standards (run in triplicate), were analysed in every batch and analytical precision for reference material was ±0.2‰ for $\delta^{15}$N and ±0.3‰ for $\delta^{18}$O.

Figure 4.1 UKGEOTRACES transect across 40°S, samples were collected in an east to west transect from Cape Town to Montevideo. Stations sampled from D357 (October –November 2010) are highlighted in yellow and samples from JC068 (December –January 2011-2012) are highlighted in red. For intercalibration, see Chapter 2.

The stoichiometric parameter N* is calculated here as NO$_3$ - 16 x PO$_4$$^{3-}$ (Gruber and Sarmiento, 1997). Proportions of remineralized and preformed phosphate were calculated using Apparent Oxygen Utilization (AOU) (AOU = [O$_2$]$_{sat}$ - [O$_2$]$_{observed}$). These were converted to NO$_3$ using organic matter respiration stoichiometry (Anderson, 1995, [PO$_4$$^{3-}$]$_{remin}$ = 1/170 * AOU; [PO$_4$$^{3-}$]$_{preformed}$ = [PO$_4$$^{3-}$]$_{observed}$ - [PO$_4$$^{3-}$]$_{remin}$).
4.4 Results

The 40°S transect captures the deep water masses which are transported through the Cape and Argentine basins (Figure 4.2). The most dense of the water masses at 40°S is the Weddell Sea Deep Water (WSDW), identified here in the Argentine basin with temperatures below <0°C (Figure 4.2). The WSDW is formed in the Weddell Sea, via cooling and brine water formation processes and sinks along the continental slope, moving northwards into the Argentine basin. Overlying this, the Lower Circumpolar Deep Water (LCDW) formed in the Antarctic Circumpolar Current (ACC) is identified by temperatures between 0-1.5°C in the Cape and Argentine basin. The WSDW and LCDW together comprise the Antarctic Bottom Water (AABW), with the dense WSDW prevented from leaving the Argentine basin due to topographic barriers. At 40°S the southward flowing NADW has been eroded by the entrainment of Southern Ocean waters (Figure 4.2). The tracer PO$_4^{3-}$ can be used to calculate the proportion of NADW at 40°S (Broecker et al., 1998). This tracer indicates ~2/3-3/4 of waters at 2500 m are of North Atlantic origin. The core of the water mass is still detectable on the Western boundary (up to 90 %) at depths of 2500 m, with temperatures and salinities of 3.1°C and 35.1 psu, respectively. The Upper Circumpolar Deep Water (UCDW), originating from the ACC, is detectable with a core at 1250 m, identified by high concentrations of macronutrients (NO$_3^-$ >31 µM) and lower O$_2$ concentrations (<180 µM) (Figure 4.3). Above the UCDW, the less dense Antarctic Intermediate Water (AAIW) and Subantarctic Mode Water (SAMW) have lower salinities, and are ventilated in the subantarctic surface. The AAIW is formed at the Subantarctic Front (SAF) and has a salinity minimum at 750 m (~34.2 psu), a consequence of high precipitation rates in formation regions at ~55°S (Talley, 1996). Overlying the AAIW is the SAMW which is formed in a deep winter mixed layer in the SE Pacific. These waters enter the Atlantic via the Drake Passage, at 40°S the core of this water mass is at 500 m detectable with low Si:N concentrations (Figure 4.3).
Figure 4.2 Temperature vs. salinity with NO$_3^-$ concentrations denoted with colour bar. The intermediate water in this transect is distinguished by a salinity minimum of the AAIW. Beneath the intermediate waters, the Southward moving NADW is evident with a salinity maximum at ~2500 m. Below the NADW, salinities and temperatures decrease, with the dense WSDW and LCDW. The WSDW is distinguished from the LCDW with lower temperatures.
Figure 4.3 Full depth transects across 40°S. Sections of a. Salinity, b. NO$_3^-$, c. AOU (AOU = [O$_2$]$_{sat}$ - [O$_2$]$_{observed}$) and d. Si*. Water masses are labelled in the Argentine basin, their position is similar in the Cape basin apart from the WSDW which is only evident in the Argentine basin.
The subsurface waters of the South Atlantic are well oxygenated with O\textsubscript{2} concentrations above \textasciitilde{}175 µM. The lowest O\textsubscript{2} concentrations and highest AOU concentrations are found in the UCDW (Figure 4.3), which has gained remineralized nutrients from the Pacific and Indian Oceans and transit within the ACC. The AAIW and SAMW have much lower AOU concentrations, as they are newly formed within the subantarctic surface.

The AABW has high macronutrient concentrations retained from formation regions with NO\textsubscript{3} typically \textasciitilde{}30 µM (Figure 4.3). The AABW can be identified with δ\textsuperscript{15}N\textsubscript{NO3} of 4.8‰ ±0.4 and δ\textsuperscript{18}O\textsubscript{NO3} of 2.0‰ ±0.2 (Figure 4.4). In contrast, low nutrient intermediate waters dilute the NO\textsubscript{3}\textsuperscript{-} concentration of NADW during formation. This lowers the δ\textsuperscript{15}N/NO\textsubscript{3}\textsuperscript{-} relationship and is distinct from Southern Ocean sourced waters. The average NADW δ\textsuperscript{15}N\textsubscript{NO3} is 4.8 ±0.2‰, which is slightly lower than the values of the overlying UCDW but similar to the underlying LCDW (Figure 4.5). The δ\textsuperscript{18}O\textsubscript{NO3} of 1.9 ±0.2‰ is not significantly different to the AABW, but is lower than the UCDW. In the NADW core, there is a noticeable increase in N* concentration, this increase correlates with an increase in salinity and a decrease in NO\textsubscript{3}\textsuperscript{-}.

In the UCDW, δ\textsuperscript{15}N\textsubscript{NO3} =\textasciitilde{}5.4‰, which is slightly enriched above deep ocean NO\textsubscript{3}\textsuperscript{-} signatures. The δ\textsuperscript{18}O\textsubscript{NO3} is also slightly enriched compared to the underlying water masses, with average values of 2.4‰. Enrichment in δ\textsuperscript{15}N\textsubscript{NO3} has been identified in previous work (Sigman et al., 2000) and has been attributed to communication with areas of denitrification. The Atlantic AAIW and the SAMW are both formed north of the Polar Front. The AAIW which forms at the Subantarctic Front (SAF) has high NO\textsubscript{3}\textsuperscript{-} concentrations, \textasciitilde{}3 µM lower than the UCDW (Figure 4.4). This slight decrease suggests partial consumption of NO\textsubscript{3}\textsuperscript{-} in the euphotic zone at ventilation, prior to its subduction. This is shown in the enrichment in δ\textsuperscript{15}N\textsubscript{NO3} and δ\textsuperscript{18}O\textsubscript{NO3} of the AAIW following an isotopic effect of ε =5‰ for NO\textsubscript{3}\textsuperscript{-} utilization (Figure 4.5). The SAMW at 40°S is within the nitricline at \textasciitilde{}500 m (Figure 4.5), demonstrating variable concentrations, which decrease towards the surface. In Rayleigh space (ln(NO\textsubscript{3}) vs. δ\textsuperscript{15}N\textsubscript{NO3}/δ\textsuperscript{18}O\textsubscript{NO3}, see Figure 4.5), δ\textsuperscript{15}N\textsubscript{NO3} falls below the utilization trend when compared to the UCDW and the AAIW. The δ\textsuperscript{18}O\textsubscript{NO3} follows a similar
trend to $\delta^{15}N_{NO_3}$, although $\delta^{18}O_{NO_3}$ is less decoupled from the Rayleigh trend. In the forthcoming sections, the NO$_3^-$ isotope signatures in these water masses will be discussed and the processes by which they originate investigated.

Table 4.1 The mean isotopic signatures in deep water masses as identified by their core depth at 40°S, which is denoted in brackets.

<table>
<thead>
<tr>
<th>Water Mass (core depth at 40°S)</th>
<th>No. of samples</th>
<th>$\delta^{15}N_{NO_3}$</th>
<th>$\delta^{18}O_{NO_3}$</th>
<th>$\Delta(15-18)$</th>
<th>Salinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSDW (4500 m)</td>
<td>20</td>
<td>4.8</td>
<td>2.0</td>
<td>2.9</td>
<td>34.7</td>
</tr>
<tr>
<td>LCDW (4000 m)</td>
<td>22</td>
<td>4.8</td>
<td>2.0</td>
<td>2.9</td>
<td>34.8</td>
</tr>
<tr>
<td>NADW (2500 m)</td>
<td>29</td>
<td>4.8</td>
<td>1.9</td>
<td>3</td>
<td>34.8</td>
</tr>
<tr>
<td>UCDW (1250 m)</td>
<td>23</td>
<td>5.4</td>
<td>2.4</td>
<td>3</td>
<td>34.5</td>
</tr>
<tr>
<td>AAIW (750 m)</td>
<td>25</td>
<td>5.9</td>
<td>3.0</td>
<td>2.9</td>
<td>34.3</td>
</tr>
<tr>
<td>SAMW (500 m)</td>
<td>24</td>
<td>6.2</td>
<td>3.4</td>
<td>2.8</td>
<td>34.6</td>
</tr>
</tbody>
</table>
Figure 4.4 Sections of a. $\delta^{15}$N-NO$_3$, b. $\delta^{18}$O-NO$_3$, and c. $\Delta$(15-18). Water mass depths are shown in Figure 4.3. Intermediate water masses show enrichments in $\delta^{15}$N$_{NO3}$ and $\delta^{18}$O$_{NO3}$.
Figure 4.5 Left panel: Comparison of water masses at 40°S in Rayleigh space. a. $\delta^{15}$N$_{NO_3}$ and b. $\delta^{18}$O$_{NO_3}$ are plotted against the natural log of nitrate. Dashed lines mark a fractionation trend of 5‰. Comparison of intermediate waters to previous work in the Southern Ocean is made with coloured crosses in each plot. Right panel: $\delta^{15}$N$_{NO_3}$, $\delta^{18}$O$_{NO_3}$ plotted against salinity. Error bars denote 2σ. Mean values for each water mass are plotted with triangles, these are calculated by the mean value from the core depth of that water mass at 40°S, see Table 4.1 for more details (AABW=>4000 m, NADW=2500 m UCDW=1250 m AAIW=750 m, SAMW=500 m).
4.5 Discussion

If all NO$_3^-$ sourced from the Southern Ocean originates from a similar source within the ACC, with no N cycling processes occurring apart from NO$_3^-$ utilization at the surface, then the isotopic fractionation can be predicted. If this were the case and each of the Southern Ocean water masses originated from the Antarctic Circumpolar Current (ACC), then samples should fall close to measured values for the UCDW/LCDW or along a Rayleigh fractionation trend (Figure 4.5). The measured water mass values for the UCDW, AAIW and SAMW are marked in Figure 4.5, with similar patterns present in the intermediate waters of the Pacific Ocean (Rafter et al., 2013). The enrichment of AAIW with decreasing concentration, gives support for partial utilization leaving enrichment in preformed NO$_3^-$ from ventilation (Sigman et al., 2000). The SAMW shows only a small enrichment for the degree of NO$_3^-$ decrease, suggesting that mixing with subtropical waters may be diluting the effect of NO$_3^-$ utilization (DiFiore et al., 2006). The NADW is clearly identifiable in Figure 4.5 as a water mass forming in contrasting conditions, with lower NO$_3^-$ compared to the Southern Ocean water masses. This water mass also has lower $\delta^{15}$N$_{NO3}$ and $\Delta(15$-18) in comparison to the UCDW and LCDW. These observations will be explored in the forthcoming discussion to disentangle the N cycling processes that leave an isotopic imprint on deep water NO$_3^-$ in this region.

4.5.1 AABW formation and transport into the South Atlantic

The AABW, which includes WSDW and LCDW, is the densest of oceanic water masses (Orsi et al., 1999); its formation is centred on the Antarctic continental margins where Circumpolar Deep Water (CDW) is entrained southward from the ACC interacting with cold and dense shelf waters (Naveira Garabato et al., 2002). This occurs within the Weddell Sea (Orsi et al., 1999), the Ross Sea and along Adelié Coast (Sloyan, 2006), with a dominance of Atlantic sources. In the western limb of the Weddell Gyre, newly formed AABW is transported northwards into the abyssal plains. At 40$^\circ$S AABW exhibits a $\delta^{15}$N$_{NO3}$ of 4.8 ±0.2‰ and $\delta^{18}$O$_{NO3}$ of 2.0 ± 0.2‰ (Figure 4.5). The isotopic signatures $\delta^{15}$N$_{NO3}$ values are comparable to those reported in the Indian and Pacific sectors of the Southern Ocean ($\delta^{15}$N$_{NO3}$ = 4.8 ±0.2‰, $\delta^{18}$O$_{NO3}$ = 1.8 ±0.2‰, Sigman et al., 2000; Sigman et al., 2009; Rafter et al., 2013).
Previous studies have attributed the isotopically lighter signature of Pacific AABW, to mixing with NADW (Rafter et al., 2013). The $\delta^{18}O_{\text{NO}_3}$ of NADW (1.9‰) is too high to produce the $\delta^{18}O_{\text{NO}_3}$ reported in the Southern Ocean AABW (1.6‰), therefore these low signatures may be produced by remineralization processes. Recent work has identified low $\delta^{18}O_{\text{NO}_3}$ in the Kerguelen Plateau area of the Southern Ocean, which has been attributed to nitrification (Dehairs et al., in press). This may suggest nitrification processes may be prevalent in some regions of the Southern Ocean, causing decreases in $\delta^{18}O_{\text{NO}_3}$ to lower values than are identified in the majority of the oceans subsurface.

4.5.2 Formation and transport of intermediate water masses in the South Atlantic

The intermediate waters which form in the subantarctic transport high concentrations of CO$_2$ and nutrients away from the surface ocean, having an important role in climate regulation (Hartin et al., 2011). These water masses can be temporally variable and a number of factors have been considered to play a role in their formation (McCartney, 1982; Piola and Gordon, 1989; Santos and England, 2004). The intermediate waters at 40°S are identified between 500-1500 m, with the upper waters ventilated in the Subantarctic Zone (SAZ).

4.1.2.1 Upper Circumpolar Deep Water

The UCDW forms the base of the intermediate waters entering the Atlantic Ocean, and contrasts from the AAIW and SAMW, as it is not ventilated in the SAZ. It is transported eastward in the ACC, formed by lateral mixing with subantarctic waters and further modified by the sinking organic matter flux in the ACC (Sigman et al., 2000). Deep waters from ocean basins add to the UCDW on its eastward circumpolar circuit to form a mixture of Atlantic, Pacific and Indian deep waters (Oudot et al., 1999). The UCDW enters the Atlantic Ocean from the Drake Passage and moves northwards above the NADW underlying the Southern Ocean ventilated AAIW and SAMW. It is identified in Figure 4.3 at ~1250 m by the oxygen minimum and high NO$_3^-$ concentrations; characteristics that signify its deep water origin from nutrient rich Pacific and Antarctic waters (Oudot et al., 1999).
The $\delta^{15}\text{N}_{\text{NO}_3}$ of UCDW reported from the Pacific/Indian sectors of the Southern Ocean is enriched to $\sim$5.5‰, attributed to the incorporation of enriched NO$_3^-$ via communication with ODZs (Oxygen Deficient Zones) (Sigman et al., 2000). A recent study measured $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ in the Pacific UCDW of 5‰ and 2‰ (Rafter et al., 2013). At 40°S, $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ are found to be enriched above typical deep ocean values to $\sim$5.4‰ and $\sim$2.4‰ respectively, supporting the incorporation of heavy $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$. The loss of NO$_3^-$ via denitrification leaves an imprint on $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ which can be transported far from the ODZ where the process occurred (Sigman et al., 2000). If mean deep ocean $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ are $\sim$5‰ and $\sim$2‰, there is an observed enrichment of 0.4‰ and 0.4‰, respectively. The enrichment in $\delta^{15}\text{N}_{\text{NO}_3}$ is similar to previous observations of the UCDW within the ACC (Sigman et al., 2000), demonstrating that the signature of denitrification can be transported far from regions of denitrification.

The $\Delta(15-18)$ of Pacific UCDW has been measured at 3‰ and appears to be unaltered by NO$_3^-$ utilization and remineralization at the Southern Ocean surface (Rafter et al., 2013), in this study the $\Delta(15-18)$ is comparable (3‰) suggesting a negligible effect of nitrification on this isopycnal. It is expected that sinking organic matter in NO$_3^-$ rich Southern Ocean surface waters would add lower $\delta^{15}\text{N}_{\text{NO}_3}$ and low $\Delta(15-18)$ to the underlying water mass through remineralization. As there is no observed decrease in $\Delta(15-18)$ during water mass transit from the Southern Ocean, the effect of remineralization on the overall water mass signature is low in comparison to the enrichment observed by denitrification in distal areas. The high nutrient concentrations in the CDW would require a large amount of remineralization to make a significant change to NO$_3^-$ isotope signatures. Thus, the high $\delta^{15}\text{N}_{\text{NO}_3}$ isotopic characteristics of the UCDW are inherited from the Pacific and Indian Oceans, transporting a denitrification signal into the Atlantic Ocean. This can be further supported by low O$_2$ and N* concentrations in the UCDW. These isotopic values identified in the UCDW can be used as a baseline for any changes within the overlying intermediate waters as a result of their formation in the Southern Ocean.
4.1.2.2 Antarctic Intermediate Water

Circumpolar Deep Water upwells close to Antarctica and flows northward via Ekman Transport as Antarctic Surface Water (AASW). AASW is progressively freshened through air-sea fluxes and sea-ice and subducts at the Subantarctic Front (SAF) to form AAIW (Talley, 1996). A number of processes affect the formation of the AAIW such as convection within the mixed layer, Ekman transport, eddy fluxes and mixing within the SAF (Oudot et al., 1999). The relative importance of the SAMW and AASW as a source for the AAIW has been disputed in previous studies (Piola and Gordon, 1989). Sigman et al., (2000) conclude that both AASW and SAMW may contribute to the formation of the SE Pacific AAIW, as a lowering of the $\delta^{15}$N/NO$_3^-$ relationship indicates incorporation of SAMW (Sigman et al., 2000).

At 40°S, NO$_3^-$ decreases from the UCDW to the AAIW, this coincides with an increase in $\delta^{15}$N/NO$_3^-$ and $\delta^{18}$O/NO$_3^-$ to 5.9‰ and 3.0‰, respectively (Figure 4.5). The enrichment in $\delta^{15}$N/NO$_3^-$ and $\delta^{18}$O/NO$_3^-$ follows an isotopic effect of ~5‰ indicating that the NO$_3^-$ decrease in this water mass is from the consumption of NO$_3^-$ by phytoplankton at the SAZ surface. This suggests that the AAIW is formed principally from the UCDW and AASW (which is formed from the UCDW). Partial NO$_3^-$ assimilation in the AASW drives increases in $\delta^{15}$N$_{NO_3}$ and $\delta^{18}$O$_{NO_3}$ along a NO$_3^-$ utilization fractionation trend. These elevations in $\delta^{15}$N$_{NO_3}$ and $\delta^{18}$O$_{NO_3}$ have been observed in the summer SAZ surface (Rafter et al., 2013), and winter mixing and formation of the AAIW drives the incorporation of elevated $\delta^{15}$N$_{NO_3}$ and $\delta^{18}$O$_{NO_3}$ into the AAIW. Although the $\Delta(15-18)$ of AAIW is comparable to the UCDW (2.9%), which indicates that isotopically lighter N added by the remineralization of organic matter from the SAZ does not significantly alter the signature (Rafter et al., 2013). The AAIW NO$_3^-$ at 40°S in the Atlantic mainly reflects surface biological utilization in formation areas close to the SAF. This suggests that the Atlantic AAIW is formed principally from the UCDW and AASW, which results in the water mass following a Rayleigh trend from the UCDW.

4.1.2.3 Subantarctic Mode Water

SAMW formation is observed in the SE Pacific north of the SAF in winter as vertical mixing of the thermocline with the SASW (Piola and Georgi, 1982). These waters
enter the Drake Passage and move northwards along the Western boundary of the South American coast via the Malvinas Current (Sloyan and Rintoul, 2001). At the Brazil-Malvinas Confluence (BMC), the SAMW is forced eastward and eventually northwards into the subtropical gyre in the Cape basin (Stramma and England, 1999). These waters circulate in the wind driven gyres and supply the subtropical regions with preformed nutrients (Palter et al., 2010; Sarmiento et al., 2004).

The subantarctic thermocline waters have a low $\delta^{15}N/NO_3^-$ relationship compared to other Southern Ocean water masses (Figure 4.5, DiFiore et al., 2006). The low $\delta^{15}N/NO_3^-$ of SAMW is too low to be explained by mixing with only Southern Ocean waters (Figure 4.5), and it has been attributed to mixing with the subtropical thermocline (Sigman et al., 2000). The low $\delta^{15}N/NO_3^-$ of the SAMW at 40°S identifies the importance of subtropical waters in the formation of the Atlantic SAMW. The subtropical thermocline of the South Atlantic has low NO$_3^-$ concentrations, but also low $\delta^{15}N_{NO_3}$ from the addition of new N, which could assist in delineating the SAMW from the Rayleigh relationship. This may also provide reasoning for the greater deviation of $\delta^{15}N_{NO_3}$ away from the Rayleigh trend compared to $\delta^{18}O_{NO_3}$, as subtropical waters have low $\Delta(15-18)$.

The $\Delta(15-18)$ of Pacific SAMW is lower than the UCDW and AAIW (Rafter et al., 2013), and may result from the sinking of low $^{15}N$ organic matter produced in surface waters, where high NO$_3^-$ concentrations allow the preferential consumption of $^{14}N$. The subsurface low $\delta^{15}N_{NO_3}$ produced from remineralized NO$_3^-$ is recycled to surface waters in winter mixing events. This seasonal cycling in which remineralized NO$_3^-$ with low $\delta^{15}N$ replenishes the SAMW may be an important component of intermediate water modification (Rafter et al., 2013). The $\Delta(15-18)$ signatures within the Atlantic SAMW are lower than the UCDW by $\sim$0.2‰. We suggest these signatures may result from remineralization processes and also mixing with the low latitude thermocline. The features of the SAMW at 40°S in the Atlantic support the mixing with low latitude waters to lower the $\delta^{15}N/NO_3^-$ relationship. This is likely to occur during winter when a deep mixed layer is formed. The lower NO$_3^-$ also increases the effect of remineralization on $\Delta(15-18)$ compared to the UCDW and AAIW.
4.5.3 Modification of intermediate waters

In general, the enrichment in $\delta^{18}$O from the processes of partial utilisation and denitrification are not expressed to a high degree in the deep ocean. This has been attributed to near complete or insignificant consumption of $\text{NO}_3^-$ in most regions of the surface ocean. As a result, recycled N in the deep ocean does not engender a large isotopic fractionation effect. The subantarctic is one of the only regions where $\text{NO}_3^-$ consumption can lead to $\delta^{18}$O enrichment in the subsurface (Figure 4.5). Nitrate recycling through the low latitude ocean can therefore be assessed, by observing how quickly this enriched signature is lost. If a proportion of the enrichment in intermediate waters formed in Southern Ocean is erased before reaching the North Atlantic, then the efficiency of nutrient consumption and remineralization can be inferred (Sigman et al., 2009). This information can increase our understanding of nutrient cycling and regeneration processes occurring in the low latitude ocean (e.g. Toggweiler et al., 1991; Jenkins and Doney, 2003; Palter et al., 2010).

At 40°S partially utilised $\delta^{18}$O exhibits a depth integrated average of 3.1‰ between a densities of 26.5 to 27.5 kg m$^{-3}$. Modification of this signature during transit within the Atlantic can be tracked by comparing water masses of the same density at 30°N (Knapp et al., 2008). At 40°S $\delta^{18}$O$_{\text{NO}_3}$ exhibits a depth integrated average of 2.9‰ between the SAMW (500m) and the UCDW (1250m) from partial utilization (Figure 4.6). The $\delta^{18}$O$_{\text{NO}_3}$ changes implicate upward mixing and algal consumption converting preformed $\text{NO}_3^-$ into regenerated $\text{NO}_3^-$, during passage through the low latitude Atlantic. This process of supply, uptake by phytoplankton and regeneration leads to the loss of isotopic enrichment evidenced at 40°S as the intermediate waters circulate in the Atlantic. This modification between 40°S and 30°N indicates much of the $\text{NO}_3^-$ pool has been recycled during transit through the Atlantic thermocline losing the preformed $\delta^{18}$O signatures inherited from its Southern Ocean formation region.
Figure 4.6 Comparison of a. δ^{15}N_{NO_3} b. δ^{18}O_{NO_3} and c. N* in the density range of 26.5 to 27.5 kg m^-3 between 40°S (Cyan) and 30°N (Orange) Atlantic Basin. In a. and b. values from this study at 40°S are compared to data from 30°N (Knapp et al., 2008). The decrease in δ^{15}N_{NO_3} and δ^{18}O_{NO_3} between 40°S and 30°N indicate recycling processes and a source of lighter N to the Atlantic thermocline. In c. N* concentrations from GEOSECS data show a clear increase in N* between 40°S and 30°N, showing the fortification of N during transit northwards.

Further investigation of isotopic signatures may bring to light more information on nutrient sources and cycling in the tropical Atlantic. The supply of nutrients to the low latitude thermocline has been investigated in previous work through the use of respiration stoichiometry (e.g. Kaehler et al., 2010). The consumption of O_2 in the process of respiration and nutrient production can indicate the extent of nutrient uptake and remineralization. This technique has limitations as the nutrient stoichiometry of O_2:NO_3^-:PO_4^{3-} is assumed. To assess the subtropical cycling of nutrients, an estimation of the change in the proportion of remineralized:total NO_3^- between 40°S and 30°N can be calculated using both stoichiometric and isotopic estimates (Figure 4.7). For stoichiometric estimates preformed and remineralized NO_3^- were calculated using AOU based on oxygen saturation (Garcia and Gordon, 1992) and a nutrient stoichiometry of O_2:NO_3^-:PO_4^{3-} -170:16:1 (Anderson and
Sarmiento, 1994). An average remineralized NO$_3^-$ of 5.84 mmol m$^{-2}$ was calculated using GEOSECS data (see supplementary material for more information).

![Graph](image)

**Figure 4.7** a. The concentration of remineralized NO$_3^-$ added to the thermocline along isopycnals is calculated at 30°N. The blue circles indicate the calculation of remineralised NO$_3^-$ concentration using Apparent Oxygen Utilization assuming a nutrient remineralization stoichiometry of -170:16:1 ($\text{NO}_3^-$ remin = (1/170 * AOU) *16). For comparison remineralized nitrate is also estimated by using the modification of $\delta^{18}$O$_{\text{NO}_3}$ from 40°S to 30°N (see Figure 4.6), the decrease in $\delta^{18}$O$_{\text{NO}_3}$ is a result of recycling processes converting preformed NO$_3^-$ to remineralised NO$_3^-$. This is calculated by $\delta^{18}$O$_{\text{NO}_3}$ = $\delta^{18}$O$_{\text{nitr}}$ x (X) + $\delta^{18}$O$_{\text{imported}}$ x (1-X). The green, red and orange crosses indicate the calculated values using $\delta^{18}$O$_{\text{nitr}}$ values of 1.4‰, 1.6‰ and 1.8‰ respectively. b. The same methods to calculate remineralized nitrate as used in a., here the proportion of NO$_3^-$ which has undergone recycling between 40°S and 30°N is calculated by NO$_3^-$ remin/NO$_3^-$ total. c. The nutrient stoichiometry of remineralized NO$_3^-$ and PO$_4^{3-}$ is calculated by comparing remineralized NO$_3^-$ estimates to estimates of remineralized PO$_4^{3-}$ from the calculation 1/170 * AOU. The blue dashed line shows the 16:1 stoichiometry assumed from nutrient remineralization concomitant with O$_2$ decreases.

The degree of recycling determined by $\delta^{18}$O is dependent on the $\delta^{18}$O of newly nitrified NO$_3^-$ ($\delta^{18}$O$_{\text{nitr}}$) through the Atlantic and is independent of assumed nutrient stoichiometry. As NO$_3^-$ is consumed by phytoplankton, this process acts as an ultimate loss of the O molecule from fixed N. During the process of nitrification $\delta^{18}$O
“resets” to lighter values of 1.1‰ plus $\delta^{18}O_{\text{H2O}}$ (Sigman et al., 2009). In the subtropical Atlantic surface waters, the $\delta^{18}O$ of water ranges between 0.3-1.5‰ (Bigg and Rohling, 2000). This would suggest newly nitrified $\text{NO}_3^-$ produced within the subtropical Atlantic would obtain a $\delta^{18}O_{\text{nit}}$ of 1.4-2.6‰. To investigate nutrient supply and modification through the subtropics, three conservative estimates of $\delta^{18}O_{\text{nit}}$ have been used (1.4, 1.6 and 1.8‰, see Table 4.2). The recycling efficiency of $\text{NO}_3^-$ was estimated by calculating the necessary amount of nitrification required to decrease $\delta^{18}O_{\text{NO}_3}$ to the measured signature at 30°N ($\delta^{18}O_{\text{meas}} = \delta^{18}O_{\text{nit}} \times (X) + \delta^{18}O_{\text{imported}} \times (1-X)$).

Table 4.2 Estimations of remineralized $\text{NO}_3^-$ using $\delta^{18}O_{\text{NO}_3}$ in the density range of 26.4 to 27.3 kg m$^{-3}$. Estimations of remineralized $\text{NO}_3^-$ at 30°N using AOU are ~5.8 mmol m$^{-2}$ assuming an $\text{O}_2$:P stoichiometry of -170/1. This value is compared to various $\delta^{18}O_{\text{nit}}$ estimates to calculate the N:P stoichiometry and new N estimates.

<table>
<thead>
<tr>
<th>Method</th>
<th>$\delta^{18}O_{\text{nit}}$ (%)</th>
<th>Remineralized $\text{NO}_3^-$ (mmol m$^{-2}$)</th>
<th>Excess N above Redfield (mmol m$^{-2}$)</th>
<th>N:P</th>
<th>New N estimate using $\delta^{18}O_{\text{NO}_3}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOU</td>
<td>n/a</td>
<td>5.8</td>
<td>n/a</td>
<td>16</td>
<td>n/a</td>
</tr>
<tr>
<td>$\delta^{18}O$</td>
<td>1.4</td>
<td>6.5</td>
<td>0.7</td>
<td>17.9</td>
<td>6</td>
</tr>
<tr>
<td>$\delta^{18}O$</td>
<td>1.6</td>
<td>7.2</td>
<td>1.4</td>
<td>20.0</td>
<td>13</td>
</tr>
<tr>
<td>$\delta^{18}O$</td>
<td>1.8</td>
<td>8.0</td>
<td>2.2</td>
<td>22.0</td>
<td>21</td>
</tr>
</tbody>
</table>

The estimations from the two methods show a large discrepancy in the proportion of remineralized $\text{NO}_3^-$ at 30°N between a density range of 26.7 and 26.9 kg m$^{-3}$ (Table 1, Figure 4.6). The isotopic estimates calculate a larger proportion of the $\text{NO}_3^-$ pool is recycled by 30°N compared to the stoichiometric approach. This decoupling may suggest a higher efficiency of supply and remineralization occurring in these water masses, which is apparent in $\delta^{18}O_{\text{NO}_3}$, but not in the AOU estimates. In Table 1, the estimates of excess N above the AOU estimates are calculated for each of the $\delta^{18}O_{\text{nit}}$ estimates. Here we estimate an increase in remineralized $\text{NO}_3^-$ of between 0.7 and 2.2 mmol m$^{-2}$ above the AOU estimates of 5.8 mmol m$^{-2}$. The AOU estimates assume a ratio of 16:1 for N:P remineralization; however, $\delta^{18}O_{\text{NO}_3}$ based estimates do not rely on assumed nutrient stoichiometry and calculate the amount of $\text{NO}_3^-$ which has
been nitrified from organic matter. The estimate from these approaches can be reconciled if N:P ratios of regeneration were higher (18-22:1). This reasoning provides a mechanism for investigating nutrient remineralization stoichiometry, as the decoupling suggests an underestimation of N:P using AOU methods. To assess the changes in nutrient stoichiometry from the $\delta^{18}$O$_{NO_3}$ method, we calculate the concentrations of remineralized NO$_3^-$ at 30°N and compare this to PO$_4^{3-}$ estimates from AOU. From this approach, using a $\delta^{18}$O$_{nit}$ range of 1.4 to 1.8 ‰, our estimates of N:P remineralization fall between 18 and 22:1 (Figure 4.7). This suggests that the Atlantic organic matter remineralization stoichiometry, integrated over 40°S-30°N, is higher than Redfield ratios. The excess N above Redfield which is added to the Atlantic thermocline can be converted to a percentage of new N. Our estimates fall within a range of 6 to 21% of NO$_3^-$ (Table 4.2).

### 4.5.4 Quantifying new N inputs to the Atlantic basin

The $\delta^{15}$N$_{NO_3}$ can be used to determine the underlying reasons for higher N:P stoichiometry. If no new N is added to the water masses in transit, then there should be no change in the $\delta^{15}$N signatures (Figure 4.6). The two profiles of $\delta^{15}$N highlight an external source of light N being added to the water column. To calculate the required addition of new N to decrease $\delta^{15}$N$_{NO_3}$, we can calculate the proportion of newly fixed N required at each density by using equation 4.1 (see also Table 4.3). Where $X =$ proportion of newly fixed N in sample.

$$\delta^{15}N_{meas} = \delta^{15}N_{N2fix} x (X) + \delta^{15}N_{imported} x (1-X) \quad (4.1)$$

For example at a density of 26.8:

$$4.2‰ = -1‰ x (X) + 7.1‰ x (1-X);$$

$$X = 1 - \frac{(4.2 - (-1))}{7.1 - (-1)} = 0.36$$

Concentration of newly fixed N = 0.36 x 12.3 = 4.42 µmol L$^{-1}$. 
Table 4.3 Average nitrate concentrations and isotopic values on the isopycnals of the upper limb of the MOC. North Atlantic data is taken from Knapp et al. (2008).

<table>
<thead>
<tr>
<th>Density (kg m$^{-3}$)</th>
<th>South Atlantic (40°S)</th>
<th>North Atlantic (30°N)</th>
<th>Newly fixed N (µmol m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NO$_3^-$ (µM)</td>
<td>δ$^{15}$N$_{NO3}$</td>
<td>NO$_3^-$ (µM)</td>
</tr>
<tr>
<td>26.5</td>
<td>5.3</td>
<td>9.3</td>
<td>4.9</td>
</tr>
<tr>
<td>26.6</td>
<td>6.3</td>
<td>8.5</td>
<td>6.7</td>
</tr>
<tr>
<td>26.7</td>
<td>8.4</td>
<td>6.3</td>
<td>10.9</td>
</tr>
<tr>
<td>26.8</td>
<td>10.1</td>
<td>7.1</td>
<td>12.3</td>
</tr>
<tr>
<td>26.9</td>
<td>13.5</td>
<td>7.1</td>
<td>14.2</td>
</tr>
<tr>
<td>27.0</td>
<td>19.1</td>
<td>6.2</td>
<td>18.1</td>
</tr>
<tr>
<td>27.0</td>
<td>22.7</td>
<td>6.3</td>
<td>20.8</td>
</tr>
<tr>
<td>27.3</td>
<td>27.5</td>
<td>6.0</td>
<td>23.7</td>
</tr>
<tr>
<td>27.4</td>
<td>30.6</td>
<td>5.8</td>
<td>26.9</td>
</tr>
<tr>
<td>27.4</td>
<td>32.1</td>
<td>5.6</td>
<td>24.9</td>
</tr>
<tr>
<td>27.5</td>
<td>34.1</td>
<td>5.5</td>
<td>22.5</td>
</tr>
<tr>
<td>27.6</td>
<td>34.2</td>
<td>5.4</td>
<td>20.3</td>
</tr>
</tbody>
</table>

An estimation of 2.6 ± mol N m$^{-2}$ of new N is added to subtropical Atlantic, which converts to 12-17% of NO$_3^-$ within this density range. The proportions calculated allow an inventory of recently fixed N in the subtropical Atlantic thermocline to be estimated. An N$_2$ fixation rate is calculated by dividing the inventory of newly fixed N by an appropriate timescale over which the recently fixed N within the thermocline has accumulated. Our estimate of 15 ±2.5% of the NO$_3^-$ inventory of 17.2 mol N m$^{-2}$ being sourced from N$_2$ fixation, converts to an estimated N$_2$ fixation rate of 26-36 Tg N yr$^{-1}$ using the model constraints outlined in Knapp et al. (2008).

This estimate of new N addition falls within our δ$^{18}$O$_{nit}$ estimates of 1.6-1.8‰, which gives confidence to our assumptions of a considerable input of new N driving a change in the N:P stoichiometry (Table 4.2). Using δ$^{18}$O estimates we calculate that between 58-73% of NO$_3^-$ is remineralized, this would suggest that ~23% of new production is fuelled by an external source of N. Using both δ$^{15}$N and δ$^{18}$O we demonstrate that an external source of N is required to reconcile both the δ$^{15}$N and δ$^{18}$O budget for the subtropical Atlantic. This suggests that there is a significant
addition of excess N to the Atlantic thermocline, which is supported by a light isotopic source.

A difference in N* of 3.3 µM has been calculated between the water masses entering and leaving the Atlantic basin, which would suggest an Atlantic N:P ratio of 19.3:1 (Moore et al., 2009). This high N:P stoichiometry is within our estimates of NO$_3^-$ input to the thermocline. A study of NO$_3^-$ isotope signatures in the North Atlantic similarly concluded inputs of new N to the Atlantic thermocline (Knapp et al., 2008). This study further concludes that the high N:P stoichiometry and light δ$^{15}$N source are added to the thermocline through remineralization. Phytoplankton other than diazotrophs cannot produce lighter N in the tropics and subtropics where NO$_3^-$ consumption is near complete in surface waters. Integrated over large temporal and spatial scales their sinking remains are expected to confirm to Redfield stoichiometry. Atmospheric deposition can be a source of light N to the surface waters but is unlikely to produce high N:P stoichiometry in sinking particles and during remineralization. This is because N released from the solubilisation of dust at the surface needs to be carried to depth through biological uptake, sinking and remineralization. Therefore, N$_2$ fixation is the only process which is likely to produce light N as well as high N:P ratios during regeneration of sinking detritus at intermediate depths.

In summary, using δ$^{18}$O we estimate increased concentrations of remineralized NO$_3^-$ in the subtropics than calculated using AOU concentrations. The NO$_3^-$ carried through intermediate waters undergoes substantial recycling in the Atlantic thermocline. In addition, the modification of δ$^{15}$N$_{NO_3}$ and δ$^{18}$O$_{NO_3}$ and the inferred high N:P ratios of regenerated nutrients suggest significant addition of new N by diazotrophs. This modification of the subtropical intermediate waters strongly suggests that the high N:P of nutrients is caused by the remineralization of high N:P detritus and that a significant component of this (26-36 Tg N yr$^{-1}$) is from new N input by diazotrophs.
4.5.5 Controls on Atlantic $N_2$ fixation

A previous nitrate isotope study in the subtropical North Atlantic estimates newly fixed N inputs between 15 and 24 Tg N yr$^{-1}$ (Knapp et al., 2008). In comparison to previously estimated Atlantic $N_2$ fixation rates, our estimates are higher than Hansell et al. (2007) (22 Tg N) and Deutsch et al. (2007) (20 Tg N). Recent work which has used N:P ratios and $N_2$ fixation rates, estimates a flux of $\sim2.1 \times 10^{12}$ mol N yr$^{-1}$, comparable to those in this study (Yoshikawa et al., 2013). In a global perspective, current estimates of global $N_2$ fixation range between 140 and 180 Tg N yr$^{-1}$ (Deutsch et al., 2007; Grosskopf et al., 2012), which would signify Atlantic estimates are 18 to 23% of global $N_2$ fixation.

In this work an Atlantic $N_2$ fixation rate of 26-36 Tg N yr$^{-1}$ is calculated. If excess P is the primary control on $N_2$ fixation rates in each basin, then this process would require an excess P supply of $\sim1.3 \times 10^{11}$ mol N yr$^{-1}$. As there is negligible N loss in the Atlantic and therefore minimal excess P production, the majority of excess P is likely to be supplied to the basin externally. Excess phosphate is supplied to the Atlantic from the Southern Ocean and Arctic Ocean (transported from the Davis Strait) (Figure 4.8). The combined estimates of these two sources can be estimated as approximately 2.8 to 4.1 $\times 10^{10}$ mol P yr$^{-1}$ from the Arctic and 4.7 $\times 10^{10}$ mol P yr$^{-1}$ from the Southern Ocean, supplying the Atlantic with $\sim 6.8-11.1 \times 10^{10}$ mol P yr$^{-1}$ in excess of Redfield requirements (Moore et al., 2009, Torres-Valdes et al., 2013). This excess P supply could support a $N_2$ fixation rate of 1.1 to 1.8 $\times 10^{12}$ mol N yr$^{-1}$ or 15.4 to 25.2 Tg N yr$^{-1}$. Estimates from this work suggest higher rates of 26-36 Tg N yr$^{-1}$.

This indicates that either more excess is supplied to or produced within the Atlantic than currently estimated or that $N_2$ fixation rates may be higher than the amount of excess P which is supplied to the Atlantic basin.

If $N_2$ fixation rates are higher than excess P supply, this would lead to progressive increases in excess N in the Atlantic, unless excess N is exported from the Atlantic. Moore et al. (2009) speculated that the majority of new N added to the North Atlantic enters the deep circulation, causing an $N^*$ divergence between the imported Southern Ocean water masses and the exported NADW. The change in $N^*$ suggests...
~1.3 x10^{12} \text{ mol N yr}^{-1} \text{ is exported from the Atlantic basin via the southward flow of the NADW (Moore et al., 2009). This estimation suggests excess N of ~1 x10^{12} \text{ mol N yr}^{-1} being added to the Atlantic basin, and not exported within the NADW. This amount is relatively similar to the estimation of excess phosphate from the Southern Ocean waters and Arctic Ocean (Figure 4.8). Approximately 44\% of the excess N that is added to the subtropical Atlantic is retained and balanced by the import of a similar amount of excess phosphate, thus not leading to a change in the stoichiometry of the inventory over time. Therefore in this work we have identified a relatively high N\textsubscript{2} fixation rate, higher than the current estimates of excess P supply to the basin, which may be the cause of excess N export from the basin and high N:P ratios. If excess P is the primary control on N\textsubscript{2} fixation, then there must be a mechanism which drives higher N fixation rates.

I propose three main mechanisms which may drive these higher inputs of new N and higher N:P stoichiometry in the North Atlantic thermocline. Firstly, the N:P stoichiometry of non N\textsubscript{2} fixers in the North Atlantic is higher than 16:1 where slow growing species such as Prochlorococcus dominate (Mills and Arrigo, 2010). The success of these species, may lead to the export of high N:P organic matter from surface waters promoting the remineralisation of excess nitrate in the thermocline. This phenomenon would create an excess of P within the Atlantic surface waters allowing higher rates of N\textsubscript{2} fixation than can be estimated from solely Redfield uptake estimates. Secondly, the high N:P stoichiometry of N\textsubscript{2} fixers exports excess N to the thermocline. For this process to occur it would suggest that organic material is directly exported from surface waters as diazotrophic matter and not further recycled through the Atlantic surface waters. Although the isotopic signature of N\textsubscript{2} fixation would be retained through recycling processes within the subtropical surface waters, the high N:P stoichiometry of diazotrophic biomass would be lost through efficient recycling. This process would therefore require a lower recycling efficiency of N\textsubscript{2} fixing species. A third factor which could drive increases in N\textsubscript{2} fixation rates above a Redfield supply of excess P may be the high Fe deposition or low denitrification rates within the Atlantic. A high Fe supply may increase the competitive advantage of either non N\textsubscript{2} fixers with higher N:P requirements. It could also enable the success
of N₂ fixers to increase as some of the high energy requirements may be negated from high Fe supply. The lack of N loss may also prevent high N:P signatures from decreasing to 16:1 within the Atlantic basin.

These factors still represent a mechanism that occurs in the Atlantic that is distinct from the Pacific as we know it, with N₂ fixation rates exceeding supply of excess P to the basin (using 16:1), leading to a net export of excess N from the basin. The Atlantic is a region where there is very little N loss and N₂ fixation remains to be an important process. Although the marine nutrient inventory remains well balanced over relatively long time scales, the Atlantic is a region where nitrate and phosphate are not balanced on subtropical gyre circulation timescales. This therefore suggests that the Atlantic is a region where perturbations in the marine N cycle, which may occur with ongoing climate change, may only lead to response on timescales of 1000’s of years.
Figure 4.8 Schematic of N isotope budget and the necessary inputs of new N to balance this budget. A necessary addition of $2.3 \times 10^{12}$ mol N yr$^{-1}$ is required to balance the northward flow of intermediate waters into the subtropical Atlantic. From this $1.3 \times 10^{12}$ mol N yr$^{-1}$ is exported as new N within the NADW. The remaining N balances the excess P fluxes into the ocean basins. This provides support for the Atlantic as a net source of N to the global ocean and not solely balancing the excess P supplied to the basin.
4.5.6 Formation of NADW and supply of nitrate to the Southern Ocean

The southward flow of NADW through the Atlantic is a vital feature of the Meridional Overturning Circulation (MOC) which ventilates the deep ocean (Rahmstorf and England, 1997). This thick, deep water layer is exported from the Atlantic and transported into the ACC, Indian and Pacific Oceans. The NADW is formed from the surface waters of the Atlantic which lose buoyancy in their northward transport and combine with high NO$_3^-$ sub polar waters. The relatively warm thermocline and intermediate waters form the upper inflow component of the MOC. The AABW component is sourced from the ocean bottom, identified as a cold, lower salinity bottom layer which extends northward through the North Atlantic into the Gulf Stream latitude, this water upwells into the southward flowing NADW above it. As waters of the NADW are principally from the Southern Ocean (21.5 Sv), we can use the proportion of intermediate waters and AABW entering the basin to estimate the nutrient properties of the newly formed NADW. The NO$_3^-$ which forms the NADW should reflect the integrated product of NO$_3^-$ from the subtropical Atlantic thermocline and the deep water sources which supply its formation.

### Table 4.4 Volume fluxes of meridional overturning circulation as taken from Moore et al. (2009) (McDonagh and King, 2005).

<table>
<thead>
<tr>
<th>Layer</th>
<th>Density</th>
<th>Volume (Sv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermediate layer</td>
<td>$26.2 &lt; \sigma_0, \sigma_1 &lt; 32.16$</td>
<td>16</td>
</tr>
<tr>
<td>AABW</td>
<td>$41.58 &lt; \sigma_3$</td>
<td>5.5</td>
</tr>
<tr>
<td>NADW</td>
<td>$32.26 &lt; \sigma_1, \sigma_3 &lt; 41.58$</td>
<td>-20</td>
</tr>
</tbody>
</table>

This can be investigated by comparing the isotopic signatures of the AABW and intermediate waters, with the NADW. Here we use 16 Sv for the influx of intermediate waters, 5.5 Sv for the AABW and 20 Sv for the export of NADW (as used by Moore et al., (2009) from 30°S in the South Atlantic). The AABW and the AAIW therefore comprise approximately 25% and 75% of the NADW volume,
converting to 70% and 30% of the preformed NO$_3^-$ component. Using $\delta^{18}$O$_{NO3}$ of these two water masses at 40°S (intermediate waters = 2.9‰, AABW= 2.0‰) we can calculate the expected $\delta^{18}$O$_{NO3}$ exported from the Atlantic NADW, but ignoring the effects of nutrient recycling within the Atlantic. This would produce $\delta^{18}$O$_{NO3}$ of newly formed NADW of ~2.3‰, which is higher than the average value measured at 40°S of 1.9‰. The process of recycling NO$_3^-$ through the low latitude Atlantic therefore decreases deep water $\delta^{18}$O$_{NO3}$ in the NADW by ~0.3‰.

The addition of low $\delta^{15}$N$_{NO3}$ to the low latitude Atlantic also decreases NADW $\delta^{15}$N$_{NO3}$. We estimate that the NADW $\delta^{15}$N$_{NO3}$ would be 5.1‰ from the mixing of 40°S water mass sources (intermediate waters = 6.1‰, AABW= 4.8‰). Instead, the addition of new N in the low latitude Atlantic, decreases $\delta^{15}$N$_{NO3}$ of the upper MOC from 5.8 to 4.8‰, thereby decreasing NADW $\delta^{15}$N$_{NO3}$ to 4.8‰. The addition of new N from intermediate waters also explains the high N* values of the NADW exported out from 40°S (Moore et al., 2009). We therefore can identify the importance of recycling processes and diazotrophy within the subtropical Atlantic in determining the NO$_3^-$ isotopic signatures in the NADW.

In the Atlantic Basin the new N source and recycling processes work to decrease both $\delta^{15}$N$_{NO3}$ and $\delta^{18}$O$_{NO3}$ (4.8‰ and 2‰ respectively) and increase N*. These modifications are reflected in the NADW, which is exported south from the Atlantic basin at 40°S. In this section, we estimate NADW $\delta^{15}$N$_{NO3}$ would be ~0.3‰ heavier without the process of N$_2$ fixation. This suggests that N$_2$ fixation in the low latitude Atlantic provides a source of low $\delta^{15}$N$_{NO3}$ and excess N which is exported by NADW to the Southern Ocean which in turn feeds into the global ocean. This reflects the imbalance between N$_2$ fixation and denitrification, and the negligible N loss particularly through water column denitrification in the Atlantic Basin.

The Atlantic UCDW retains a signature of denitrification, with heavy $\delta^{15}$N$_{NO3}$ and low N* which is also evident in the SE Pacific sector of the Southern Ocean (Figure 4.5, Sigman et al., 2000). At 40°S, UCDW has an initial N* of -3.6 µM at 1500 m at 40°S suggesting a ~3.6 µmol L$^{-1}$ deficiency in N relative to P. This has important implications to water mass pathways through which denitrification and N$_2$ fixation
are coupled in the ocean. The UCDW is upwelled at the Polar Front forming the upper ACC and subsequently intermediate and mode waters. Mode and intermediate waters, sourced from the UCDW are the primary supply of nutrients to the subtopics accounting for ~75% of nutrients to subtropical export production (Palter et al., 2010). Although isotopic signatures of intermediate and mode waters are modified after upwelling of the UCDW through partial nitrate utilization and mixing processes in the Southern Ocean, they retain the N deficit inherited from the UCDW.

The water mass pathway suggested here, linking areas of N loss with subtropical thermocline waters routed through the Southern Ocean explains why N$_2$ fixation can be supported in the Atlantic basin, where minimal N loss is occurring locally. This observation is consistent with recent suggestions that large scale transport of excess P drives Atlantic N$_2$ fixation (Moore et al., 2009; Straub et al., 2013). We estimate N fixation accounts for 6-21% of NO$_3^-$ within the subtropical Atlantic thermocline. Although the majority of N$_2$ fixation is likely to occur in the Pacific and Indian Oceans; Atlantic is unique as a source of excess N to the global ocean exported through the NADW. Global atmospheric N input to the ocean from anthropogenic sources may account for ~1/3 of external fixed N supply, highlighting the significant increases in N supply to the global ocean (Duce et al., 2008). In addition to this, future climate warming is expected to increase ocean anoxia, which may expand ODZs (Bopp et al., 2002). With large perturbations in marine N cycling predicted for the forthcoming centuries, this work suggests that Atlantic Ocean perturbations may only be balanced on longer timescales of ocean circulation.
4.6 Conclusions

This study presents the first nitrate isotope data from the South Atlantic; allowing the communication of N cycling processes between the Atlantic basin and the global ocean to be investigated. The intermediate waters which enter the Atlantic are formed from the UCDW, which carries slightly enriched signatures from denitrification regions in the Pacific. The AAIW NO$_3^-$ isotope properties can be simply explained by nutrient utilization in surface waters at the Polar Front and the SAMW is further influenced by mixing with subtropical waters. These water masses transport enriched $\delta^{15}$N$_{NO_3}$ and $\delta^{18}$O$_{NO_3}$ and low N* waters into the low latitude Atlantic. The modification of intermediate waters is identified by decreases in $\delta^{15}$N$_{NO_3}$ and $\delta^{18}$O$_{NO_3}$ from 40°S to 30°N. Using $\delta^{18}$O$_{NO_3}$ and nutrient stoichiometry we identify a fortification in N over P in the intermediate waters of the subtropical Atlantic. The modification of $\delta^{15}$N$_{NO_3}$ and $\delta^{18}$O$_{NO_3}$ and the inferred high N:P ratios of regenerated nutrients suggest significant addition of new N by diazotrophs. I estimate this as an N$_2$ fixation rate of 2.3 x10$^{12}$ mol N yr$^{-1}$. This study offers the first isotopic estimate of the water masses that enter and exit the Atlantic via the South Atlantic Ocean, as such allowing basin wide estimates to be made. I further test our N$_2$ fixation rate estimates to its export from the North Atlantic. Here I estimate an export of 1.3 x10$^{12}$ mol N yr$^{-1}$ of newly fixed N within the NADW, which is comparable to previous estimates. These modified intermediate waters supply NADW formation, which have light $\delta^{15}$N$_{NO_3}$ in comparison to the PDW and the UCDW in the Southern Ocean. The distinct $\delta^{15}$N$_{NO_3}$ in the Atlantic and Pacific Ocean may suggest an imbalance in the processes of N$_2$ fixation and water column denitrification in these basins. We posit that the UCDW which forms the base of the intermediate waters imported to the basin, carries a signature of denitrification and supplies low N:P signatures to the basin. This excess P is likely to be important in driving the observed Atlantic N$_2$ fixation, which can only be balanced on timescales of ocean circulation.
5 A global synthesis of ocean nitrate isotope measurements

5.1 Abstract

The deviation between N and O isotopes of nitrate (Δ(15-18)) can be used to determine the δ\(^{15}\)N of remineralised nitrate added to the ocean interior. In this study the isotopic signatures in remineralised nitrate through the Atlantic and Pacific basins is used to quantify the relative importance of pelagic denitrification and N\(_2\) fixation. Higher Δ(15-18) is observed in the Pacific compared to the Atlantic, which is attributed to pelagic denitrification. Indo-Pacific N\(_2\) fixation rates are required to be approximately two times the rates of pelagic denitrification to balance the isotopic composition of nitrate measured. Using published pelagic denitrification rates, this is calculated as 92-116 Tg N yr\(^{-1}\) in the Pacific and 24-32 Tg N yr\(^{-1}\) in the Indian Ocean. Combined with estimates of Atlantic N\(_2\) fixation of 26-36 Tg N yr\(^{-1}\), a global N\(_2\) fixation rate of 142-184 Tg N yr\(^{-1}\) is calculated. This work suggests that the majority of global N\(_2\) fixation is well coupled to N loss on a basin scale (~82%). However Atlantic N\(_2\) fixation rates are fuelled by the supply of excess P from the Pacific and Southern Ocean, highlighting an imbalance in the Atlantic basin scale N budget. This work supports recent work that excess P controls N\(_2\) fixation rates, yet the high rates in the Atlantic suggest the global N inventory is only fully balanced on time scales of ocean circulation.
5.2 Introduction

Marine diazotrophs add fixed N to the ocean in significant amounts to counteract the loss of N from pelagic and sediment denitrification. At present it is not fully constrained as to whether these two processes are in balance. Some researchers have found that the sinks of ocean fixed N strongly exceed sources (Codispoti et al., 2001; Codispoti, 2007), which may be explained by anthropogenic activity, increasing the extent of N loss. However the majority of recent studies find the marine N budget is relatively balanced albeit with large uncertainties (Gruber and Sarmiento, 1997; DeVries et al., 2012; DeVries et al., 2013). These views are also supported by geochemical estimates which suggest that the marine N budget has been in balance for the last 3000 years (Deutsch et al., 2004). At present our understanding of the fluxes of N\textsubscript{2} fixation and denitrification are limited by the large range in uncertainties. To address this, a variety of methods of estimation are required.

Through the use of isotopic constraints it has long been suggested that rates of benthic denitrification are larger than the loss of N via pelagic denitrification. These estimates first suggested that the ratio of water column:benthic denitrification was 1:4 (Brandes and Devol, 2002; Sigman et al., 2009b), although changes in the approaches of modelling estimates have decreased this number down to ~1:1.3-2.3 (DeVries et al., 2013). Water column denitrification occurs in suboxic waters and significant amounts of N loss occur in the Arabian Sea (Naqvi, 1987) and the Eastern Tropical Pacific (e.g. Sigman et al., 2005). Benthic denitrification occurs in most sediments with highest rates occurring close to areas of high organic matter production and low O\textsubscript{2} concentrations, such as continental margins (Devol, 2008). The rates of N loss in the water column are the principal mechanism which lead to enrichment of subsurface nitrate $\delta^{15}$N, and thus can be used to constrain N loss. The relative importance of the two main areas of oceanic N loss has been disputed, with estimates now converging on $\sim$41-63 Tg N yr$^{-1}$ for the Eastern Tropical Pacific (Deutsch et al., 2001; DeVries et al., 2012; DeVries et al., 2013) and $\sim$12-41 Tg N yr$^{-1}$ for the Arabian Sea (Devol et al., 2006; DeVries et al., 2012; DeVries et al., 2013).
It has long been regarded that the success of diazotrophs is closely linked to warm, sunlit waters (Karl et al., 2002; Mahaffey et al., 2005) but their growth is also limited by the availability of nutrients. Both P and Fe are essential for the growth of \(\text{N}_2\) fixers, although the relative influence of both in determining diazotroph distributions is still currently disputed (Deutsch et al., 2007; Ward et al., 2013; Weber and Deutsch, 2014). Also recent work suggests that diazotrophs may add significant N in high nutrient and benthic environments (Knapp et al., 2010). Using modelling of nutrient stoichiometry, it has been suggested that \(\text{N}_2\) fixers are closely linked to regions of excess phosphate relative to nitrate (\(P^*\)) (Deutsch et al., 2007; Eugster and Gruber, 2012). With this method, rates of \(\text{N}_2\) fixation in the Pacific have been suggested to be \(~6\)x the rates occurring in the Atlantic and argue against high \(\text{N}_2\) fixation occurring in the North Atlantic. Inter-basin estimates using \(P^*\) contrast those of iron supplied through atmospheric dust deposition, suggesting that the supply of iron may not be a primary limiting factor. Fe deposition rates within the Atlantic appear to drive the differences in diazotroph abundance between the North and South Atlantic (Fernandez et al., 2010; Moore et al., 2009). A recent modelling study suggests that although Fe and P are both important, Fe is the principal determinant of diazotroph abundance (Ward et al., 2013). It has also been suggested that phosphate is the primary driver of inter-basin differences, but Fe controls the variability within each basin (Weber and Deutsch, 2014).

If excess phosphate is indeed the primary driver for \(\text{N}_2\) fixation, this further supports the theory of hypothesised negative feedback in the N budget, where any external increase or decrease in fixed N is counteracted by an increase or decrease in the rate of \(\text{N}_2\) fixation. Determining the importance of basin scale \(\text{N}_2\) fixation rates may help to disentangle the relative importance of these nutrients in determining the success of diazotrophs. This is vital for our understanding of the coupling of N addition and N loss and how quickly a perturbation in the N budget is rebalanced.

The current estimations of Atlantic \(\text{N}_2\) fixation rates are \(~15-35\) Tg N yr\(^{-1}\) (Gruber and Sarmiento, 1997; Knapp et al., 2008; Moore et al., 2009; Grosskopf et al., 2012), indicating that the majority of \(\text{N}_2\) fixation occurs in the Indo-Pacific. However the range of estimates for the Atlantic remains large and the fraction of global \(\text{N}_2\)
fixation occurring in the Atlantic poorly constrained. The Atlantic is a region which may decouple N addition and N loss and could perturb the marine N budget on timescales of 100s to 1000s of years (Moore et al., 2009). It is therefore important to constrain the relative importance of N\textsubscript{2} fixation within each basin to better constrain the ability of the marine N cycle to balance on different timescales. The North Atlantic has long been thought of as a region of significant new N input relative to N loss, based on different methods such as isotope mass balance (Knapp et al., 2008; this study), N* measurements (Gruber and Sarmiento, 1997; Moore et al., 2009; Yoshikawa et al., 2013) and incubation experiments (Grosskopf et al., 2012; Moore et al., 2009). High dust input to the North Atlantic has been found to fuel N\textsubscript{2} fixation in this region and prevent high N\textsubscript{2} fixation in the phosphate rich South Atlantic (Michaels et al., 1996; Falkowski, 1997; Moore et al., 2009). However recent work identifying hydrogen supersaturations in the South Atlantic may point to a higher abundance of unicellular diazotrophs than previously estimates (Moore et al., 2014). A recent modelling study using excess phosphate data found insignificant N\textsubscript{2} fixation rates in the Atlantic, which they attributed to coarse horizontal resolution (Eugster and Gruber, 2012). When adopting a budget approach, Atlantic rates increased from \(~0-3\) Tg N yr\(^{-1}\) to 30 Tg N yr\(^{-1}\). The variability in modelled and measured rates from current work in the Atlantic highlights the large uncertainties around N\textsubscript{2} fixation rates suggesting a variety of methods are required to reduce the uncertainty.

The variability of nutrient demands by phytoplankton can lead to under or overestimations of N\textsubscript{2} fixation using Redfield estimates (Mills and Arrigo, 2010). High N demand by non diazotrophs such as Prochlorococcus and Synechococcus may increase the availability of phosphate to diazotrophs in the North Atlantic and increase the estimates of N\textsubscript{2} fixation. In a similar way denitrification may be underestimated by an amount proportional to the sinking flux and the remineralisation of high N:P organic matter from the surface. Therefore, non-Redfield nutrient utilisation by non diazotrophs can decouple the processes of N\textsubscript{2} fixation and denitrification and therefore the steady state inventory. Reduction in excess phosphate by diatoms and the corresponding decrease in N\textsubscript{2} fixation may explain the apparent imbalance between N\textsubscript{2} fixation and N loss. This highlights the
need to use isotopic signatures on a global scale as an added constraint to nutrient stoichiometry. The isotopic signature of remineralised NO$_3^-$ added to each ocean basin may provide constraints on the relative importance of N$_2$ fixation and denitrification in each basin. In this chapter N$_2$ fixation rates in each ocean basin are estimated using stable isotope methods to consider the relative coupling between N fixation and N loss in each basin.

As an increasing amount of $\delta^{15}$N$_{NO_3}$ and $\delta^{18}$O$_{NO_3}$ data emerges from the literature, the spatial gradients of both $\delta^{15}$N and $\delta^{18}$O can be used to examine the effects of N cycling processes on the composition of nitrate in the ocean interior. Sub surface NO$_3^-$ makes up the vast proportion of the global fixed N budget, and can be used to constrain the processes of N addition and loss. In this chapter $\delta^{15}$N$_{NO_3}$ and $\delta^{18}$O$_{NO_3}$ are used to investigate remineralisation processes and the relative magnitudes of N sources and sinks to the marine budget. With better constraints of subsurface $\delta^{18}$O$_{NO_3}$, a higher precision of N and O dynamics can be used to assess fluxes of N$_2$ fixation and denitrification by utilisation of the tracer $\Delta$(15-18). $\Delta$(15-18) can be used to assess the relative importance of N$_2$ fixation and denitrification to remineralised NO$_3^-$ and the magnitude of new N input in different basins.
5.3 Nitrate N and O isotope Data

$\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$ data has been collected from a number of published sources (Sigman et al., 2005; Difiore et al., 2006; Knapp et al., 2008; Rafter et al., 2013; U. Tsunogai; Geotraces International Data Product) and compiled for an inter-basin comparison. Additional samples analysed for this study were collected from the South Atlantic, the Atlantic sector of the Southern Ocean and the Arctic Ocean (Figure 5.1). The Arctic Ocean and Southern Ocean samples were collected onboard the RRS James Clark Ross. Arctic Ocean samples were collected on cruise JR271, between June – July 2012 and Southern Ocean samples were collected on cruise JR274 between January and February 2013. Sample collection and analysis by the Denitrifier Method was carried out using methods described in Chapter 2. The isotope data was compiled in conjunction with biogeochemical measurements of nutrient stoichiometry ($N^*/P^*$) and the concentrations of remineralised and preformed nutrients. The stoichiometric parameters $N^*$ and $P^*$ are calculated using Equations 5.1 and 5.2. Apparent Oxygen Utilisation is calculated using Equation 5.3. $O_2^{'} = O_2$ saturation, or the oxygen the water mass would have if the water were in equilibrium with the atmosphere, at the temperature and salinity of the water mass. Proportions of remineralised and preformed phosphate were calculated using Apparent Oxygen Utilisation (AOU), as described in Equations 5.4 and 5.5. These were converted to NO$_3^-$ using organic matter respiration stoichiometry (Anderson, 1995). All concentrations in Equations 5.1-5.5 are expressed in $\mu$mol L$^{-1}$. Western and eastern profiles for the Atlantic were averaged from full depth profiles within the Cape and Argentine basins, SE Atlantic from Stations 2-6 and SW Atlantic from Stations 13-21.

\[ N^* = NO_3^- - 16 \times PO_4^{3-} \] (5.1)
\[ P^* = PO_4^{3-} - 16 / NO_3^- \] (5.2)
\[ AOU = O_2^{'} - O_2 \] (5.3)
\[ [PO_4^{3-}]_{\text{remin}} = 1/170 \times AOU \] (5.4)
\[ [PO_4^{3-}]_{\text{preformed}} = [PO_4^{3-}]_{\text{observed}} - [PO_4^{3-}]_{\text{remin}} \] (5.5)
Figure 5.1 A global map of the locations of nitrate isotope measurements used in this study. The additional samples analysed from this work are from the South Atlantic, Weddell Gyre and subantarctic Southern Ocean and the Arctic Ocean. The rest of the measurements have kindly been supplied by Patrick Rafter, Angela Knapp and the Geotraces International Data Product (U. Tsunogai).
5.4 Results and Discussion

5.4.1 N$_2$ fixation and denitrification

It has long been recognized that the principal input of new NO$_3^-$ to the ocean is via N$_2$ fixation and loss via denitrification. Pelagic denitrification enriches both $\delta^{18}$O and $\delta^{15}$N above their sources of nitrification (O) and N$_2$ fixation (N). If the sources of N and O atoms were similar, both $\delta^{15}$N and $\delta^{18}$O should be enriched to the same degree above their newly nitrified values of $\sim$-1‰ and $\sim$1‰. Instead $\delta^{18}$O is much lower in the deep ocean, as regeneration through nitrification resets $\delta^{18}$O$_{NO3}$ to its nitrification source. $\delta^{15}$N$_{NO3}$ represents a balance between loss via denitrification and input via N$_2$ fixation with a mean of 5‰ as nitrate recycling retains N molecules and has little effect on remineralised $\delta^{15}$N. The decoupling of $\delta^{15}$N and $\delta^{18}$O can be used to look at the relative importance of the two processes of nitrate isotope enrichment and to distinguish between the overlapping processes of N$_2$ fixation and pelagic denitrification. Pelagic denitrification has a large isotopic effect during N consumption of 25‰ and leaves residual nitrate heavily fractionated. This process works to increase the $\delta^{15}$N of subsurface nitrate above its input value of $\sim$1‰ from N$_2$ fixation. In the Atlantic, there is no significant water column denitrification. Therefore the signature of N$_2$ fixation is dominant on newly produced nitrate and is likely to be retained until homogenised within the deep ocean reservoir. In contrast, high $\delta^{15}$N$_{NO3}$ from denitrification may overprint the role of N$_2$ fixation in other ocean basins.

A general trend of increasing $\delta^{15}$N and $\delta^{18}$O is observed when the processes of denitrification and partial utilization are occurring in each ocean basin (Figure 5.2). In the North Atlantic, $\delta^{15}$N$_{NO3}$ decreases towards the surface in the subtropical waters causing samples to fall away from the 1:1 values of deep ocean nitrate of 5‰ and $\sim$1.8‰. $\delta^{15}$N decreases towards the surface, whilst $\delta^{18}$O increases, leading to a trajectory perpendicular to the expected trend for NO$_3^-$ loss. This results from a combination of total assimilation by phytoplankton, no pelagic denitrification and nitrogen fixation within the basin.
In a recent study of the Pacific Ocean, low Δ(15-18) signatures were observed in both the north and south subtropical gyres (although to a larger extent in the north subtropical gyre) (Rafter et al., 2013). These signatures were attributed to remineralisation of newly fixed material. Similar results have also been identified at Hawaii Ocean Time series (HOT) (Knapp et al., 2011, Figure 5.2). In the Pacific, contrasting trends of increases in δ¹⁵N relative to δ¹⁸O are observed from the remineralisation of high δ¹⁵N, whereas δ¹⁸O signatures are lost. In the Eastern Pacific ODZ, there is a trend to lighter Δ(15-18) with increasing δ¹⁵N which has been observed as changes in Δ(15-18) concomitant with denitrification preceding (Sigman et al., 2005; Figure 5.2, orange diamonds falling off 1:1 trajectory with increasing enrichment). It has been suggested that newly fixed N could be causing this change (Sigman et al., 2009a), however redox cycling of nitrate can lead to a branching mechanism where δ¹⁸O gets increasingly enriched compared to δ¹⁵N. In recent work using the isotopic constraints of NO₂⁻ in addition to NO₃⁻ it has been inferred that
Redox cycling appears to be the dominant mechanism in driving this change in ODZs (Casciotti and McIlvin, 2007; Casciotti et al., 2013). This mechanism for changing low latitude $\Delta(15\text{-}18)$, may complicate its use in identifying the relative influence of $N_2$ fixation and denitrification to the remineralised component close to ODZs.

$\delta^{15}N_{NO_3}$ in the Atlantic decreases by the addition of new N to the low latitude surface and the lack of pelagic denitrification. The NADW exported from the Atlantic therefore has low $\delta^{15}N_{NO_3}$ of $\sim$4.7 to 4.9‰ and $\delta^{18}O_{NO_3}$ of $\sim$1.7-1.9‰. The Atlantic is unique in that water column denitrification does not play a significant role in the N cycling within this basin. In Figure 5.3 the gradients $\delta^{15}N_{NO_3}$ in the Atlantic and Pacific are shown. The lighter values in the Atlantic are evident in comparison to the Pacific Ocean. Here average subsurface values (taken as below 2000 m) are $\sim$4.8‰ in comparison to $\sim$5 and 5.2‰ in the Pacific. As partial utilisation appears to affect all basins in a similar manner with an input of enriched $\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$ from the subantarctic, this is unlikely to cause variation in $\Delta(15\text{-}18)$. The difference in the subsurface of the different ocean basins may be a consequence of the net effects of $N_2$ fixation and denitrification as these processes determine the N inventory and can change the isotopic signatures.
Figure 5.3 Comparison of the gradient in $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and $\Delta(15\text{-}18)$ in the Atlantic and Pacific Oceans. Higher $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ are observed in the Pacific within the subsurface in comparison to the Atlantic. The gradient appears to be more for $\delta^{15}\text{N}$ than for $\delta^{18}\text{O}$ suggesting that the remineralised component within the Atlantic has a lighter N than the Pacific.

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Over large enough time and space scales, redox cycling processes should be relatively insignificant as the overall addition of new N and loss of N via denitrification are large enough (≈180 Tg N yr⁻¹) to have a dominant effect on subsurface NO₃⁻. As noted in previous work, the δ¹⁵N of mean deep ocean NO₃⁻ should represent a balance between the N₂ fixation and pelagic denitrification (Sigman et al., 2009b). As the whole ocean volume turnover time is on the timescale of ~1000 years, this represents a turnover time of ≈1/3 to 1/4 of the marine N inventory within one circulation of the global ocean. This serves as an explanation for the slight variation of δ¹⁵NNO₃ observed in different basins, as the full marine N reservoir is not homogenised within each basin. The Antarctic Circumpolar Current (ACC) within the Southern Ocean acts as a mixer of waters from the Atlantic (with lighter δ¹⁵N and higher N*) and the Indo-Pacific (with heavier δ¹⁵N and lower N*) (Figures 5.3 and 5.4). In these ocean sections there is a clear change in the deep waters from lower δ¹⁵N in the Atlantic to higher δ¹⁵N in the Pacific. Some of the high δ¹⁵N may be from advected NO₃⁻ which has communicated with heavy NO₃⁻ close to the ODZs of the Pacific. To separate out remineralised nitrate from preformed nitrate, the Δ(¹⁵-₁⁸) signatures can be used. The Δ(15-18) distribution below 2000 m increases from 3-3.2‰ in the Atlantic to 3.2-3.4‰ in the Pacific (Figure 5.3). Nitrate below ~2000 m in each ocean basin should represent the sum of the waters being transported into the basin via deep water transport and the integrated value of the remineralised product within that basin. The change in the integrated product should represent a balance between the relative fluxes of N₂ fixation and denitrification within each basin. Remineralised NO₃⁻ therefore must either increase in δ¹⁵N or decrease in δ¹⁸O from the Atlantic to the Pacific. To look at this in greater detail I focus now on the deviations between the N and O isotopes of nitrate using the parameter Δ(15-18).
Figure 5.4 The same Atlantic to Pacific gradient is shown here as is shown in Figure 5.3, with a. $N^*$ concentrations, b. preformed nitrate and c. remineralised nitrate. Here there is a clear gradient between $N^*$ and distance, with much higher $N^*$ concentrations in the Atlantic in comparison to the Pacific. The two sources of preformed nitrate are identified in the middle panel, with higher concentrations in the Pacific and Southern Oceans in comparison to the Atlantic. Remineralised nitrate is added in transit, with an increased concentration from Atlantic to Pacific.
To explore variations in $\Delta(15-18)$, profiles of $\delta^{18}O_{NO_3}$ and $\Delta(15-18)$ are compared at 40°S in the Pacific and Atlantic basins to assess the waters imported and exported. $\delta^{18}O$ trends are remarkably similar in both basins (Figure 5.5), $\delta^{18}O_{NO_3}$ is enriched in the subantarctic water masses and values of $\sim 1.8\%o$ are typical for most of the subsurface. This suggests that nitrification adds $\delta^{18}O_{NO_3}$ with a relatively homogenous signature in the Atlantic and Pacific basins. In the Pacific $\Delta(15-18)$ between 1000-3000 m is $\sim 3.4\%o$, whereas in the Atlantic it is $\sim 3\%o$ consistently throughout this depth range. This suggests that the average remineralised $\delta^{15}N_{NO_3}$ in the Pacific is higher than that of the Atlantic. Profiles from 30°N are further compared to those from 40°S in both of these basins (Figure 5.6). In the Atlantic, as intermediate waters are transported northwards into the low latitudes, $\Delta(15-18)$ decreases, whereas in the Pacific the $\Delta(15-18)$ increases. This implicates the addition of lighter $\delta^{15}N_{NO_3}$ in the Atlantic compared to the Pacific.

The deep waters also follow a similar pattern, but with the waters masses moving south (Figure 5.6). These contrasting features show that remineralised nitrate in the
Atlantic acts to decrease $\Delta(15-18)$ both in the intermediate waters and the deep waters and in the Pacific remineralised nitrate acts to increase $\Delta(15-18)$. As the $\delta^{18}O_{NO_3}$ profiles are similar for the Atlantic and the Pacific at 40°S, $\Delta(15-18)$ variation can be attributed to $\delta^{15}N_{NO_3}$. The predicted $\Delta(15-18)$ in the Indian Ocean can therefore be calculated using measured $\delta^{15}N_{NO_3}$ data from ~40°S in the Indian Ocean. This assumes a mean $\delta^{18}O_{NO_3}$ of the Pacific and Atlantic and uses $\delta^{15}N_{NO_3}$ from 40°S in the Indian Ocean. In Figure 5.5 this is demonstrated and the estimated $\Delta(15-18)$ is very similar to that of the Pacific. The similarity between the Indian and Pacific $\delta^{15}N_{NO_3}$ data (DiFiore et al., 2006; Rafter et al., 2013), allows us to compare the Atlantic to the Indo-Pacific to determine the overriding influences of pelagic denitrification and N$_2$ fixation on nitrate imported and exported from each ocean basin.

![Graph showing $\Delta(15-18)$ profiles at 30°N and 40°S in the Atlantic and Pacific basins. Arrows indicate the direction of water movement. In the two basins there is an opposite change in $\Delta(15-18)$ in water mass flow. In the Pacific $\Delta(15-18)$ increases, whereas in the Atlantic $\Delta(15-18)$ decreases.](image_url)
5.4.2 Estimating causes of $\delta^{15}$N variation

To investigate the marine N budget further, $\Delta(15-18)$ variability within the Atlantic and Pacific Oceans is assessed to indicate the extent to which remineralised nitrate is adding low or high $\delta^{15}\text{N}_{\text{NO}_3}$ to the subsurface. Subsurface nitrate below 2000 m is used, as this comprises the majority of ocean nitrate and provides an integrated view of variable surface processes. The amount of remineralised NO$_3^-$ increases as deep waters are transported through the Atlantic and Pacific Oceans. The concentration and source of preformed and remineralised NO$_3^-$ will affect the nitrate isotope signature exported from each basin in deep water masses. I track the change in nutrients using mass balance to determine the fraction of preformed NO$_3^-$ transported into the basin and the required $\Delta(15-18)$ of remineralised NO$_3^-$ ($\Delta(15-18)_{\text{remin}}$) added to the ocean interior (Figure 5.4, Table 5.1).

### Table 5.1 Estimates of the integrated values of remineralised nitrate in the Pacific and Atlantic basins. Preformed and remineralised nitrate are calculated using WOCE data.

<table>
<thead>
<tr>
<th>Ocean Region</th>
<th>Preformed $\mu$mol L$^{-1}$</th>
<th>Remin. $\mu$mol L$^{-1}$</th>
<th>$%$ Remin.</th>
<th>$\Delta(15-18)$ meas. ($%$)</th>
<th>$\Delta(15-18)$ remin. ($%$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Atlantic</td>
<td>15</td>
<td>0</td>
<td></td>
<td>$3.2 \pm 0.15$</td>
<td></td>
</tr>
<tr>
<td>South Atlantic</td>
<td>18.5</td>
<td>$7 \pm 2$</td>
<td>$27 \pm 6$</td>
<td>$3 \pm 0.1$</td>
<td>$2.5 (1.7-2.9)$</td>
</tr>
<tr>
<td>Southern Ocean</td>
<td>29</td>
<td>12.7</td>
<td></td>
<td>$3.2 \pm 0.2$</td>
<td></td>
</tr>
<tr>
<td>Pacific</td>
<td>22</td>
<td>$23 \pm 2$</td>
<td>$23 \pm 4$</td>
<td>$3.4 \pm 0.2$</td>
<td>$4.1 (3.2-4.95)$</td>
</tr>
</tbody>
</table>

Preformed nitrate sourced from the North Atlantic and Southern Ocean is constrained as ~15 and ~29 $\mu$M respectively. The proportion of NO$_3^-$ added to each basin is calculated using WOCE data. The $\Delta(15-18)_{\text{remin}}$ required to increase or decrease the $\Delta(15-18)$ to the measured value is calculated using Equation 5.5. For the Atlantic, the decrease of 0.2‰ requires an input of ~2.6‰ of $\Delta(15-18)_{\text{remin}}$. For the Pacific a $\Delta(15-18)_{\text{remin}}$ of ~4.1‰ is required. The precision of measurements and the implications of this on estimates were explored and are added in parentheses in Table 5.1. For the Atlantic, isotope errors ranged between 1.7 and 2.8‰ and for the concentrations between 2.3 and 2.6‰. For the Pacific they ranged between 3.2 and 5‰ for isotopes and 4 and 4.2‰ for the concentrations.
\[ \Delta(15-18)_{\text{hot}} = \Delta(15-18)_{\text{remin}} \times f_{\text{remin}} + \Delta(15-18)_{\text{pre}} \times f_{\text{pre}} \]  

\( \Delta(15-18)_{\text{remin}} \) estimates can be used to calculate the fraction of remineralised \( \text{NO}_3^- \) that is sourced from \( \text{N}_2 \) fixation. The relative proportion of pelagic denitrification and \( \text{N}_2 \) fixation will determine the \( \delta^{15}\text{N} \) of remineralised nitrate added to each basin. Using published estimates of pelagic and benthic denitrification fluxes in each basin, the necessary addition of newly fixed N can be explored. In doing so, I separate the Atlantic basin from the Indo-Pacific. The total pelagic denitrification can be used to calculate the necessary addition of newly fixed N to the Indo-Pacific. This approach utilises estimates of water column denitrification occurring in the Indo-Pacific and the ratio of this to benthic denitrification.

Figure 5.7 Schematic of model. The nitrate pool loses N via water column and sedimentary denitrification. Fixed N is added by \( \text{N}_2 \) fixation and the integrated remineralised product represents a balance between these two processes.
In this section I use published estimates of 180 Tg N yr\(^{-1}\) for total denitrification and 66 Tg N yr\(^{-1}\) for water column denitrification (DeVries et al., 2012). If 1/3 of the fixed N pool is perturbed over one circulation of the global ocean, this would constitute 1/3 loss of fixed N via denitrification and 1/3 addition via N\(_2\) fixation (Figure 5.7). Of this \(\sim\)1/3 is via pelagic denitrification (66/180) within the Indo-Pacific which would lead to a loss of \(\sim\)11% of NO\(_3^-\) via water column denitrification and an increase in \(\delta^{15}\)N\(_{NO3}\) to 7.9‰. The remineralised product would be \(\delta^{15}\)N minus \(\delta^{18}\)O (7.9 - 1.8‰) and a \(\Delta(15-18)\)\(_{\text{rem}}\) of \(\sim\)6.1‰. Using a balanced NO\(_3^-\) budget with 180 Tg of N loss and input, a flux of 133-149 Tg of newly fixed N is required to the Indo-Pacific for modelled \(\Delta(15-18)\)\(_{\text{rem}}\) to equal measured \(\Delta(15-18)\)\(_{\text{rem}}\) (Figure 5.8). Even with changes in the approach used (Appendix 6), the average amount of Indo-Pacific N\(_2\) fixation still requires \(\sim\)130-150 Tg N yr\(^{-1}\), with a loss of 66 Tg N yr\(^{-1}\) from the water column, or approximately double the N\(_2\) fixation compared to pelagic denitrification. This converts to a N\(_2\) fixation rate of 82-126 Tg N yr\(^{-1}\) for the Pacific basin and 24-82 Tg N yr\(^{-1}\) for the Indian basin. These N\(_2\) fixation rates balance the isotopic constraints of remineralised \(\delta^{15}\)N as evidenced by the tracer \(\Delta(15-18)\).

Figure 5.8 Modelling the estimated nitrogen fixation rates in the Indo-Pacific and Atlantic basins. Indo-Pacific best estimates are \(\sim\)140 Tg N yr\(^{-1}\), assuming a balanced budget.
Table 5.2 shows the estimated denitrification rates of DeVries et al. (2013), combined with N\textsubscript{2} fixation estimates from this work. Using this isotopic approach the inputs and outputs in the global ocean are balanced, supporting the most recent literature of a balanced marine N cycle (Gruber, 2004; DeVries et al., 2012). Further information can be drawn from the spatial variability of N inputs and losses. The calculations of the relative importance of N\textsubscript{2} fixation in each of the three ocean basins falls close to the estimates of Deutsch et al. (2007) and Weber and Deutsch, (2014), where the Pacific is the most dominant basin for N\textsubscript{2} fixation and the Indian and Atlantic basins contribute a lesser amount. The inputs and outputs from the Indian and Pacific basins are in balance albeit with uncertainties. The Atlantic however has a higher input of new N to the basin than the amount that is lost via benthic denitrification. This is identified by the observed change in N\textsuperscript{*} signatures exported within the NADW (Chapter 4, Moore et al., 2009). New N exported from the Atlantic may be necessary in balancing the loss of N from the Southern Ocean via benthic denitrification (Table 5.2). New N which is exported from the Atlantic will be mixed into the ACC and a proportion of N may be lost via denitrification in sediments. This may present a reason why there is no significant excess N added to the Pacific Ocean (Weber and Deutsch, 2014). It also may indicate importance in the supply of excess N from the Atlantic to offset loss in the global ocean.

<table>
<thead>
<tr>
<th>Pelagic Denitrification</th>
<th>Benthic Denitrification</th>
<th>N\textsubscript{2} fixation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atlantic</td>
<td>0</td>
<td>16</td>
</tr>
<tr>
<td>Pacific</td>
<td>50</td>
<td>42</td>
</tr>
<tr>
<td>Indian</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Southern Ocean</td>
<td>0</td>
<td>26</td>
</tr>
<tr>
<td>Total</td>
<td>60</td>
<td>104</td>
</tr>
</tbody>
</table>
This work indicates a balance of N inputs and losses in the Indian and Pacific basins but that the Atlantic adds excess N to the Southern Ocean which may counteract Southern Ocean N losses. It has long been observed that mean deep ocean nitrate is ~5‰ in the Southern Ocean, with little variation from this in the rest of the global ocean. I find that the Atlantic adds $\delta^{15}\text{N}_{\text{NO}_3}$ of ~4.8‰ and the Pacific adds $\delta^{15}\text{N}_{\text{NO}_3}$ of ~5.2‰. As the NADW represents ~50% of deep waters, then this balances the slight increases that occur in the other ocean basins. I therefore conclude that the different basins are relatively in balance with one another in terms of N inputs and losses, but the isotope budget and Atlantic imbalances are only balanced via mixing within the Southern Ocean.

### 5.4.3 Assessing the controls on basin-wide N$_2$ fixation

Estimations from this work suggest the global fluxes of N$_2$ fixation and denitrification are relatively balanced. This work further supports recent publications that the majority of N$_2$ fixation occurs in the Indo-Pacific (Eugster and Gruber, 2012; Weber and Deutsch, 2014). If pelagic denitrification accounts for approximately half of N$_2$ fixation rates in these basins, then this would implicate rates of 92-116 Tg N yr$^{-1}$ in the Pacific and 24-32 Tg N yr$^{-1}$ in the Indian Ocean. Recent work suggests that excess P is the overall basin wide control over N$_2$ fixation rates and that Fe determines the spatial variability (Weber and Deutsch, 2014). Fe requirement may cause diazotroph distribution in the Pacific to be relocated westward of denitrification regions into the subtropical gyres (Weber and Deutsch, 2014). Fe limitation therefore may not prevent diazotrophs from fully compensating the upwelled N deficit, but more it may determine where in the basin it occurs. The coupling of feedbacks on a basin-scale is sufficient to produce strong stabilising feedbacks from the shallow circulation pathways.

However estimates of N$_2$ fixation in the Atlantic basin are supported by an external supply of excess P (Chapter 4, Deutsch et al., 2007). This external supply via intermediate waters of the Southern Ocean and from the Arctic Ocean does not provide a mechanism by which negative feedbacks can respond quickly to perturbations in the marine N cycle. Here the two processes remain imbalanced with
an excess of P imported to the basin and an excess of N exported. As such, global N$_2$ fixation and denitrification are uncoupled to some degree due to these discrepancies in the Atlantic.

Although excess P may be the primary determinant of the relative extent of N$_2$ fixation within each basin (highest in the Pacific), N$_2$ fixation rates may be difficult to quantify this from nutrient stoichiometry alone. As identified in Chapter 4, N$_2$ fixation estimates are higher than the external supply of excess P to the Atlantic. This may occur from a build-up of excess P \textit{in situ} from non N$_2$ fixing species and/or a low recycling efficiency (and higher export) of diazotroph material. Alternatively the high Fe supply and low denitrification rates may lead to a higher N:P stoichiometry of phytoplankton in the North Atlantic. If the Atlantic supports ~26-36 Tg N yr$^{-1}$ of N$_2$ fixation, excess Fe within the basin may influence the success of diazotrophs. The North Atlantic provides an environment, in which high levels of Fe are deposited and the dominant diazotroph, \textit{trichodesmium} proliferates. The ability for this species to control its buoyancy may promote the higher recycling efficiency of P than is currently considered in model estimates (Karl et al., 2002, Yoshikawa et al., 2013). Recent work also suggests a significant presence of unicellular diazotrophs in the South Atlantic which may result in higher rates of N$_2$ fixation than previously thought from rate measurements alone (Moore et al., 2014). If there are higher rates in the South Atlantic than previously inferred, this could suggest that the species \textit{trichodesmium} may work to add more fixed N to the marine reservoir in the presence of high Fe concentrations (i.e. the North Atlantic).

At present we cannot distinguish between the importance of Fe and excess P in controlling to Atlantic N$_2$ fixation. In recent work it was found that adding Fe to the marine reservoir does not dramatically change the N reservoir but decreasing Fe supply by 25% could lead to a decrease of 40% of oceanic fixed N (Weber and Deutsch, 2014). Denitrification would decrease with decreasing export of newly fixed N but the ocean could still lose >25% of its N reservoir (Weber and Deutsch, 2014).
Clearly more work is required to assess the areal rates of N$_2$ fixation, which may help to determine the importance of Fe and P in controlling global N$_2$ fixation. In this study, the Pacific is estimated to support the majority of global N$_2$ fixation, which is balanced by the significant N loss from this basin. This work suggests that the majority of N gain and loss within the ocean is balanced on a basin scale, as the N isotope signatures suggest relative homogeneity in these processes. This work continues from the work of Chapter 4 to further assess the importance of N$_2$ fixation on a global scale. Estimations of global N$_2$ fixation rates using nitrate isotope data suggest N$_2$ fixation and denitrification are balanced on a global scale. The majority of N$_2$ fixation occurs in the Indo-Pacific, therefore is well coupled to N loss on shorter time scales of basin circulation. As most of global N$_2$ fixation is coupled within each basin to N loss this suggests that these dynamic processes are relatively coupled globally providing a mechanism by which the marine N cycle has remained relatively balanced over the last few thousand years. The Atlantic is distinct from the Indo-Pacific, as the majority of N$_2$ fixation is supported by an external supply of excess P to the basin. Therefore the Atlantic basin is a region where negative feedbacks to perturbations in the marine N cycle may only occur on timescales of ocean circulation (1000’s years).
5.5 Conclusions

Through the increased availability of nitrate isotope data it is possible to further test assumptions about the fractionation of N and O isotopes in the ocean interior in terms of the residence time of nitrate within the subsurface ocean. The isotopic signature of remineralised nitrate added to the ocean subsurface is estimated through the Indo-Pacific. Low $\Delta(15-18)_{\text{remin}}$ in the Atlantic and high $\Delta(15-18)_{\text{remin}}$ in the Pacific demonstrating contrasting N cycling in the two basins. Balancing the nitrate isotope budget of the Indo-Pacific requires $N_2$ fixation rates to be double the rates of pelagic denitrification. This study therefore estimates $N_2$ fixation rates of 92-116 Tg N yr$^{-1}$ in the Pacific and 24-32 Tg N yr$^{-1}$ in the Indian Ocean. Combined with Atlantic Ocean $N_2$ fixation estimates of 26-36 Tg N yr$^{-1}$, a global N fixation rate of 142-184 Tg N yr$^{-1}$. This provides support that the basin wide extent of $N_2$ fixation is somewhat determined by the amount of P supply, providing a means by which N loss and gain are balanced on a global scale. Nutrient stoichiometry alone may not provide accurate basin wide fixation estimates and that isotope studies can further improve these estimates to overcome differences problems tied to nutrient stoichiometry.
6 Carbon isotope fractionation in marine phytoplankton across the South Atlantic subtropical front

6.1 Abstract
The stable isotopic composition of particulate organic carbon ($\delta^{13}$C$_{POC}$) in surface waters has been found to vary systematically with CO$_2$$_{aq}$ in the global ocean (e.g. Rau et al., 1989). Other factors such as surface area to volume ratios of phytoplankton, cell shape and carbon concentrating mechanisms have been found to decouple this observed correlation and argue against its use as a palaeoproxy. In this study I test $\delta^{13}$C variability in the South Atlantic subtropical convergence (SSTC) to determine the range in carbon isotope fractionation ($\varepsilon_p$) by phytoplankton. South of the SSTC and across most of the open Southern Ocean, $\delta^{13}$C$_{POC}$ correlates with CO$_2$ and growth rates, as determined by phosphate concentrations. I hypothesise that high CO$_2$$_{aq}$ and low carbon fixation determine the extent of $\varepsilon_p$ in the subantarctic waters as found in most regions of the Southern Ocean. In contrast, I find that $\delta^{13}$C$_{POC}$ in the subtropical regions is principally affected by cell size of algal assemblages. I suggest that smaller cell sizes increase the efficiency of carbon uptake and increase $\varepsilon_p$. I observe no evidence for the use of carbon concentrating mechanisms in phytoplankton within these regions. This work argues against the use of $\delta^{13}$C$_{POC}$ as a palaeoproxy for pCO$_2$ and finds lower $\delta^{13}$C$_{POC}$ in subtropical regions than previous studies. This may in part be from increases in CO$_2$$_{aq}$ and decreases in $\delta^{13}$C$_{CO2}$, but also could result from increased $\varepsilon_p$, suggesting phytoplankton may already be changing to a higher CO$_2$ environment.
6.2 Introduction

During photosynthesis by marine phytoplankton, aqueous CO₂ (CO₂[aq]) is taken up and converted to organic carbon (C). In this process the lighter isotope (¹²C) is preferentially consumed, leaving the residual pool increasingly enriched in the heavier isotope. The stable carbon isotopic composition of marine phytoplankton is determined by the surrounding environmental conditions which supply carbon to the cell and the algal cell physiology. Therefore the δ¹³C of marine plankton in the surface ocean can be influenced by the isotopic composition of the carbon source, any fractionation during carbon fixation and further modification during reactions within the organism. The δ¹³C of particulate organic carbon (δ¹³C_POC) varies over relatively large oceanic areas and can be inversely correlated to CO₂[aq] (the principal carbon source) in surface waters (Sackett et al., 1965; Rau et al., 1989; Rau et al., 1991). High concentrations of CO₂[aq] can lead to greater discrimination against ¹³C as the light isotope is preferentially consumed by phytoplankton. The low temperature waters of the Southern Ocean and high saturation of CO₂[aq] lead to negative δ¹³C_POC excursions in marine plankton. From these observations, it has been assumed that CO₂[aq] availability/concentration is one of the major factors controlling δ¹³C_POC (Hayes et al., 1989; Rau et al., 1989). This has led to the use of δ¹³C_POC as a proxy to reconstruct surface water CO₂[aq] and thus atmospheric CO₂ concentrations of past climates (Freeman and Hayes, 1992; Jasper et al., 1994).

Other factors such as phytoplankton growth rate, cell size and shape and the use of carbon concentration mechanisms (CCMs) have also been identified as important in the determination of δ¹³C_POC in surface waters (Francois et al., 1993; Bidigare et al., 1997; Popp et al., 1999). Their importance decouple the observed relationship between δ¹³C_POC and CO₂[aq] and affect its use as a reliable palaeoproxy. This is particularly true in areas where CO₂[aq] is less variable, as other factors have been found to be more important for determining the degree of isotopic fractionation (Popp et al., 1998; Lourey et al., 2004; Henley et al., 2012). Phytoplankton growth rate has been shown to be a significant factor whereby higher rates of primary production result in an increased C demand and hence a restriction of isotopic fractionation (Villinski et al., 2000; Henley et al., 2012). Laws et al.(1995) suggested
that growth rate is proportional to the net transfer of CO₂ into the phytoplankton cell, assuming passive diffusional transport. The fluxes of CO₂ into and out of the cell are a function of surface area, cell wall permeability and availability of CO₂ (Laws et al., 1995). It has been demonstrated that cell geometry affects isotopic fractionation due to its control on surface area: volume ratios (Popp et al., 1998). The carbon fixation pathway can vary amongst species through the assimilation of bicarbonate via active transport: when CO₂[aq] falls below a critical level, this process has been identified to enrich δ¹³C_POC (Popp et al., 1998). CCMs occur in most cyanobacteria, increasing CO₂ at the site of Rubisco activity (Raven et al., 2008). In general, more negative excursions in δ¹³C_POC are associated with diffusive entry of CO₂, whereas CCMs or diffusive limitation of C supply lead to more positive δ¹³C_POC (Raven et al., 2008).

Although a number of factors have been observed to fractionate δ¹³C_POC in different regions of the ocean, the mechanisms which determine the variation are relatively unexplored. It is therefore important to investigate the conditions in different oceanic regions under which particular factors determine δ¹³C_POC variability. I assess the importance of CO₂[aq], cell size and phytoplankton speciation on δ¹³C_POC across a productive region of the South Atlantic Ocean. Variations in CO₂[aq] range from 10 to 15 µmol L⁻¹ in the surface waters, giving a high enough degree of variation in which its effect on δ¹³C_POC can be explored. In addition, this region supports a wide range of phytoplankton and the importance of cell size and shape and physiological mechanisms can be investigated. Finally, the mechanisms which drive δ¹³C_POC variability in this study are compared to other regions of the open ocean. A full transect across 40°S captures the productive frontal region of open ocean through the course of the spring bloom. This highly productive region is a dynamic environment with the convergence of water masses from the subantarctic and the subtropical gyre, where the processes which affect δ¹³C_POC can be difficult to constrain. Here I use a multi proxy approach to determine the variability of δ¹³C_POC. The parameters CO₂[aq], δ¹³C_DIC, δ¹⁵N_PN, Chi-a and species data are used collectively to disentangle the processes which fractionate δ¹³C_POC across this region. An overview of the processes that fractionate δ¹³C_POC in different regions of the ocean will be discussed and the mechanisms which cause this variation.
6.3 Methods

6.3.1 POC, and $\delta^{13}$C$_{POC}$ analysis

Particulate samples were collected onto ashed, pre-weighed GF/F microfibre filters (0.7 µm pore size, 25 mm diameter). Two to four litres of water were collected from the biological rosette in the surface 400 m depending on chlorophyll levels detected by the CTD fluorometer. The samples were pressure filtered simultaneously using a compressor (at ~10 psi) and an 8-way manifold system. Once the total volume for each depth was filtered, the filters were rinsed with Milli-Q water, extracted from the filter holder, placed in labelled aluminium foil and dried at 50 °C for ~12 hours. Once dried, filters were folded and stored in plastic sample bags at -20 °C. To remove carbonates prior to analysis, filters were wetted with Milli-Q water, fumed with 70% HCl for 48 hours in a desiccator, dried at 50 °C and then folded into tin capsules. The filters were analysed using a Carlo Erba NA 2500 elemental analyser in-line with a VG PRISM III isotope ratio mass spectrometer for elemental POC/PN and $\delta^{13}$C$_{POC}$ and $\delta^{15}$N$_{PN}$. Isotopic values were corrected using PACs and acetenilide standards, and POC/PN ratios were converted to µmol L$^{-1}$ using suspended particulate matter (SPM) data (See Chapter 2).

6.3.2 Ocean carbonate system

Measurements of total CO$_2$ (TCO$_2$) and total alkalinity (TA) were carried out at sea. All samples were analysed within 24 hours of collection (average time 11 hours). Samples were warmed in a water bath at 25 °C for an hour before analysis. A set volume of the sample is acidified by addition of excess 10% phosphoric acid, which converts all inorganic C species to CO$_2$. This is carried into the coulometric cell by an inert carrier gas (CO$_2$-free N$_2$ that is first passed through a magnesium perchlorate and Ascarite II scrubber), and a coulometric titration determines the amount of CO$_2$, which is equal to TCO$_2$. Small increments of 0.1 M hydrochloric acid are added to the sample and the amount added to reach the carbonic acid equivalence point is equal to the TA. Regular measurements of both TCO$_2$ and TA were made from batch 114 Certified Reference Material (CRM) from A. G. Dickson (Scripps Institution of Oceanography) and used to calibrate the results for each session. To obtain the final results in units of µmol kg$^{-1}$, a correction for density ($\rho$) due to salinity ($S$) variation
was then applied using salinity measured from Niskin bottle samples (Zeebe et al., 2001). Precision was monitored by 5-6 consecutive measurements of the same batch of water from the underway nontoxic seawater supply, carried out several times throughout the cruise. Duplicate samples were taken from the same Niskin bottle and analysed consecutively.

### 6.3.3 $\delta^{13}$C$_{\text{CO}_2}$

Samples for the measurement of the stable isotopes of C in dissolved inorganic carbon ($\delta^{13}$C$_{\text{DIC}}$) were collected from the stainless steel rosette. Samples were taken into 250 mL glass bottles with ground glass stoppers. Water was drained directly into the sample bottle using silicone tubing to the bottom of the bottle to eliminate bubble formation. The bottle and cap were rinsed once with water from the rosette bottle before overflowing the sample bottle by at least 1 bottle volume before withdrawing the silicone tube, carefully avoiding bubble formation. The stopper was then placed in the bottle and then removed so that 2.5 mL of sample could be removed to allow for thermal expansion, and 50 mL of 100% HgCl$_2$ added to halt any biological activity. The stoppers and the inside of the neck of the bottles were dried before the stopper, coated with vacuum grease, was replaced and secured with a foam insert and plastic cover. The samples were then shaken to disperse the HgCl$_2$ and stored at 4 °C until analysis. Samples were measured using a Thermo MAT253 stable isotope mass spectrometer at the University of Cambridge.

$\delta^{13}$C$_{\text{CO}_2}$ was determined from $\delta^{13}$C$_{\text{DIC}}$ and absolute temperature ($T_k$), using the following equation taken from Rau et al. (1996):

$$\delta^{13}\text{C}_{\text{CO}_2} = \delta^{13}\text{C}_{\text{DIC}} + 23.644 - 9701.5/T_k \quad (6.1)$$

### 6.3.4 High Pressure Liquid Chromatography (HPLC)

Between 500 and 1000 ml of seawater was filtered through 25 mm GF/F filters. The filters were placed in 2 ml cryovials and flash frozen in liquid nitrogen. Filters were then transferred to a -80 °C freezer for long-term storage. Pigment extracts were analysed using a reverse-phase HPLC column using Thermo-separations and Agilent instruments at the University of Oxford (Barlow et al., 1997). Phytoplankton
pigments were extracted in 2 to 5 ml 90% acetone by ultrasonication and centrifugation. Extracts were loaded into a Thermo Separations autosampler (capable of cooling pigment extracts to 2°C) and mixed with 1 M ammonium acetate (1:1, v/v) prior to injection onto a Shimadzu HPLC system (dual LC-GB pumps; SCL-6B controller). Pigments are detected by absorbance at 440 nm using a Shimadzu SPD-6AV spectrophotometric detector, and identified by retention time and on-line visible spectroscopy using a Waters 990 diode array detector. The separate pigments were separated into the size classes of micro-, nano- and pico-plankton, following equations 6.2-6.5 (Uitz et al., 2008). Where wDP = the weighted sum of the concentrations of the seven pigments.

\[ f_{\text{micro}} = \frac{1.41[\text{fucoxanthin}] + 1.41[\text{peridinin}]}{\text{wDP}} \]  
\[ f_{\text{nano}} = \frac{0.60[\text{alloxanthin}] + 0.35[\text{19'-BF}] + 1.27[\text{19'-HF}]}{\text{wDP}} \]  
\[ f_{\text{pico}} = \frac{0.86[\text{zeaxanthin}] + 1.01[\text{Chlb +divinyl – Chlb}]}{\text{wDP}} \]  
\[ \text{wDP} = 1.41[\text{fucoxanthin}] + 1.41[\text{peridinin}] + 0.60[\text{alloxanthin}] + 0.35[\text{19'-BF}] + 1.27[\text{19'-HF}] + 0.86[\text{zeaxanthin}] + 1.01[\text{Chlb +divinyl – Chlb}] \]
6.4 Results

The samples from across the Subtropical Front fall into two major nutrient regimes. The Sub Antarctic Surface Water (SASW) lies south of the front, characterised by high macronutrients and iron (Fe) limitation, while the subtropical waters north of the front display low macronutrients and nitrogen (N) limitation (Browning et al., 2014). The three subtropical water masses (Agulhas Current (AC), South Atlantic Central Water (SACW) and Brazil Current (BC)) are identified with warmer temperatures and higher salinities (Figure 6.1). Higher CO$_2$[aq] is associated with the lower temperatures of the SASW. $\delta^{13}$C$_{CO2}$ follows a negative correlation with CO$_2$[aq], with lighter isotopic signatures associated with higher CO$_2$[aq] and lower temperatures (Figure 6.1). $\delta^{13}$C$_{POC}$ across 40°S displays a predominantly marine signal with values ranging from -25 to -20‰ in the surface waters.

Satellite images of surface chlorophyll concentrations across this region indicate elevated standing stocks of phytoplankton in comparison to the South Atlantic gyre and subantarctic waters further south (Browning et al., 2014). Chlorophyll concentrations peak between austral spring and summer, and the south subtropical convergence (SSTC) moves further south as a result of the expansion of the Agulhas and Brazil Currents. The subantarctic waters have elevated and uniform chlorophyll concentrations (Figure 6.2; 0.2-0.9 mg m$^{-3}$). In the subtropical waters a deep chlorophyll maximum is observed, surface concentrations are low (<0.2 mg m$^{-3}$) and elevated concentrations are found at depth. POC largely follows Chi-a concentration, with the highest concentrations between 0 and 20°W and co-occurring with the deeper chlorophyll maximum identified in the SACW. Higher POC/chi-a is identified on the western boundary suggesting addition of POC from terrestrial sources. The marine isotopic and stoichiometric signatures indicate that the majority of suspended organic matter is produced by in-situ biological production.
Figure 6.1 Transects of temperature, absolute salinity, CO$_2$[aq], $\delta^{13}$C$_{CO_2}$ and $\delta^{13}$C$_{POC}$. Higher values are displayed in red and lower values are shown in blue. The subtropical waters are evident with high temperatures and high salinities. The influence of the Rio Plata is clear on the western boundary with lower salinities. High temperature waters correlate with lower CO$_2$[aq] and heavier $\delta^{13}$C$_{CO_2}$. $\delta^{13}$C$_{POC}$ is more variable across the transect.
Figure 6.2 Transects of chlorophyll-a and POC concentrations across the 40°S. POC and Chl-a correlate across the transect, with higher concentrations consistent through the mixed layer of the SASW and deep chlorophyll maximum evident in the subtropical water masses.

If $\delta^{13}$C$_{POC}$ were determined principally by changing CO$_2$[aq], the processes of photosynthesis in phytoplankton cells would take place by passive diffusion. The data from this study can be compared to modelled estimates for how $\delta^{13}$C$_{POC}$ is likely to be affected by changes in CO$_2$[aq], temperature or cell size. In this study, a model construction is taken from Rau et al. (1996) – Equation 6.2 and Table 6.1, which predicts the C isotope fractionation and abundance of $\delta^{13}$C$_{POC}$ where the process of photosynthesis is strictly based on the passive diffusion of CO$_2$ into marine phytoplankton cells. Here $\delta^{13}$C$_{POC}$ is determined when temperature, cell radius, cell growth rate and cell membrane permeability to CO$_2$ are specified. This approach therefore allows us to test the applicability of the CO$_2$ diffusion mechanism on $\delta^{13}$C$_{POC}$ variability.
\[ \delta^{13}\text{C}_{\text{POC}} = \delta^{13}\text{C}_{\text{CO}_2} - \varepsilon_f + (\varepsilon_f - \varepsilon_d) \frac{Q_s}{\text{CO}_2[\text{aq}]} (r/D_T + 1/P) \] (6.6)

Where \( \delta^{13}\text{C}_{\text{CO}_2} \) is the carbon isotopic composition of \( \text{CO}_2[\text{aq}] \), \( \varepsilon_f \) = intracellular enzymatic isotope fractionation, \( \varepsilon_d \) = Diffusive isotope fractionation of \( \text{CO}_2[\text{aq}] \) in seawater, \( Q_s = \text{CO}_2 \) uptake rate per unit cell surface area , \( \text{CO}_2[\text{aq}] = \text{ambient CO}_2[\text{aq}] \) concentrations, \( r = \text{cell radius} \), \( D_T = \text{temperature dependent diffusion rate of CO}_2 \) (m\(^2\) s\(^{-1}\)), and \( P = \text{cell wall permeability to CO}_2[\text{aq}] \) (Rau et al., 1996, for more information, see Table 6.1). This allows us to test whether it is likely that passive diffusion is the main mechanism for the transport of C into the cell and whether \( \text{CO}_2[\text{aq}] \) is predictable across the transect.

**Table 6.1 Description of model parameters with the values and units used. For further details see Rau et al. (1996).**

<table>
<thead>
<tr>
<th>Model parameter</th>
<th>Model output (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta^{13}\text{C}_{\text{CO}_2} )</td>
<td>Model output (‰)</td>
</tr>
<tr>
<td>( \varepsilon_f )</td>
<td>25 (‰)</td>
</tr>
<tr>
<td>( \varepsilon_d )</td>
<td>0.7 (‰)</td>
</tr>
<tr>
<td>( Q_s )</td>
<td>≈0.22 (µmol C m(^{-2}) sec(^{-1})) (dependent on ( r ))</td>
</tr>
<tr>
<td>( \text{CO}_2[\text{aq}] )</td>
<td>Temperature derived ( \text{CO}_2[\text{aq}] ) (µmol L(^{-1}))</td>
</tr>
<tr>
<td>( r ) (surface area equivalent cell radius)</td>
<td>Cell radius (µm)</td>
</tr>
<tr>
<td>( D_T )</td>
<td>5.019 x 10(^{-6}) e(^{(\varepsilon_f / kT)}) (m(^2) s(^{-1}))</td>
</tr>
<tr>
<td>( P )</td>
<td>10(^{-4}) (m s(^{-1}))</td>
</tr>
</tbody>
</table>

To test the assumption that \( \text{CO}_2[\text{aq}] \) plays a dominant role in the determination of \( \delta^{13}\text{C}_{\text{POC}} \) in surface waters across the frontal region, the relationships between \( \delta^{13}\text{C}_{\text{POC}}, \delta^{13}\text{C}_{\text{CO}_2}, \) and \( \text{CO}_2[\text{aq}] \) were investigated and compared to modelled estimates for passive diffusion (Figure 6.3). The observed distribution is different for the subtropical and subantarctic waters which are separated in Figure 6.3. \( \text{CO}_2[\text{aq}] \) and \( \delta^{13}\text{C}_{\text{CO}_2} \) in the SASW have a highly significant negative correlation \( (r=-0.77, n=12, p=0.003) \), this is expected as the concentration of \( \text{CO}_2[\text{aq}] \) should determine the \( \delta^{13}\text{C}_{\text{CO}_2} \), with lower concentrations leading to heavier \( \delta^{13}\text{C}_{\text{DIC}} \) and \( \delta^{13}\text{C}_{\text{CO}_2} \). In subtropical waters, six samples are decoupled from this trend; these samples can be
observed in Figure 6.1 with heavy δ\textsuperscript{13}C\textsubscript{CO\textsubscript{2}}, likely linked to the Rio Plata outflow. δ\textsuperscript{13}C\textsubscript{POC} and CO\textsubscript{2[aq]} in the SASW shows a negative correlation (although not significant to p<0.05) and fall close to the modelled estimates (r=-0.44, n=16, p=0.088; Figure 6.3). Subtropical samples decouple from the modelled trend to a higher degree with no significant correlation. The relationship between δ\textsuperscript{13}C\textsubscript{POC} and δ\textsuperscript{13}C\textsubscript{CO\textsubscript{2}} in the surface waters south of the front shows an insignificant positive correlation (r=0.60, p=0.114, n=8). These data suggest that although CO\textsubscript{2[aq]} may play a part in determining the δ\textsuperscript{13}C\textsubscript{POC} south of the front, other factors are likely to cause the variation away from a significant correlation. The subtropical waters are decoupled from the expected trends in Figure 6.3.

To investigate the impact of temperature on δ\textsuperscript{13}C\textsubscript{POC}, all three measurements (CO\textsubscript{2[aq]}, δ\textsuperscript{13}C\textsubscript{CO\textsubscript{2}} and δ\textsuperscript{13}C\textsubscript{POC}) were plotted against longitude and compared to model estimates based on temperature alone (Figure 6.4). The δ\textsuperscript{13}C\textsubscript{POC} measurements that fall farthest from the modelled estimates are predominantly located in the subtropical waters and especially close to the eastern and western boundaries.
Figure 6.3 Correlations between CO$_{2\text{aq}}$, δ$^{13}$C$_{\text{POC}}$, and δ$^{13}$C$_{\text{CO}_2}$. Black closed circles show samples from SASW and grey triangles subtropical surface waters. Black and grey lines show the trend line for the two regimes. The grey dashed line demonstrates the expected trend with diffusive uptake of C by phytoplankton.
Figure 6.4 $\delta^{13}\text{C}_{\text{POC}}$, $\delta^{13}\text{C}_{\text{CO}_2}$ and CO$_2$[aq] vs longitude. Closed circles show measured values and dashed line show modelled values derived from temperature. Orange = 5 m, Blue = 20 m. Yellow shaded areas denote subtropical waters and white indicates subantarctic waters.

From High Pressure Liquid Chromatography analysis (HPLC) estimations are made on the predominance of pico-, nano- and micro-plankton across the transect, which gives an indication of the variability in cell sizes (Figure 6.5). Picoplankton are abundant in the subtropical water masses, with nano and microplankton more dominant in the SASW and close to the Malvinas Current. A high concentration of microplankton is also dominant close to the western continental boundary. Changing the cell radius parameter within the model affects the relationship between $\delta^{13}\text{C}_{\text{POC}}$ and temperature (Figure 6.6). Increasing cell size reduces C isotope fractionation and increases $\delta^{13}\text{C}_{\text{POC}}$. SASW measurements fall between the modelled estimates for a cell radius of 25-30 µm. The subtropical samples have higher proportions of
picoplankton; therefore the average cell size is likely to be lower. A smaller cell size will increase surface area to volume, increasing fractionation ($\varepsilon_p$) and decreasing $\delta^{13}C_{POC}$ from the expected temperature (and CO$_2$[aq]) trend. This is demonstrated by subtropical samples (grey triangles) falling closer to smaller cell size estimates.

Figure 6.5 The size fractions of phytoplankton in surface waters as calculated from High Pressure Liquid Chromatography. The size classes are defined as fpico < 2 µm, fnano = 2 – 20 µm and fmicro = 20 – 200 µm. ‘f’ signifies the fraction of the total chlorophyll, made up of that size class.
Figure 6.6 $\delta^{13}$C$_{POC}$ versus temperature, with the modelled estimates for cell radii of 20 - 30 µm. Black closed circles = SASW, Open triangles = Subtropical waters. This graph demonstrates that a large amount of variability can be explained by changes in cell size if the use of a diffusive uptake holds.

The influence of cell size was further investigated by estimating the average cell radius for each surface sample using the relative proportion of pico, nano and micro plankton. This is a simplification as the cell radius is likely to be variable between and within phytoplankton species, but allows a preliminary assessment of correlations between cell size and $\delta^{13}$C$_{POC}$. Average cell sizes of 50 µm (micro), 10 µm (nano) and 1 µm (pico) have been adopted for this purpose. The average cell radii were compared to $\delta^{13}$C$_{POC}$ (0-40 m) and highly significant positive correlations were observed (Figure 6.7, r=0.74, n=30, p<0.001). This suggests that cell size may be one of the main factors influencing $\delta^{13}$C$_{POC}$ across the transect and can explain the variability in the SASW in Figure 6.3. The samples on the western boundary with lower salinities of the Rio Plata region were not included as they show a significant offset from this relationship (Figure 6.7). These samples have a larger cell size compared to measured $\delta^{13}$C$_{POC}$ and are under the greatest influence from the Rio
Plata outflow. Even so, independently they show a positive correlation with cell size, although this is not considered significant to $p<0.05$ ($r=0.925$, $n=4$, $p=0.075$).

The biomass of different algal groups has been analysed by HPLC techniques. These measurements indicate the proportion of chlorophyll in a sample that is sourced from different phytoplankton assemblages. Different algal groups have been identified to uptake C with varying isotopic fractionation (e.g. Henley et al., 2012). This therefore may be an additional factor which would influence the $\delta^{13}$C$_{POC}$ distributions. To test this hypothesis, the different algal groups as determined by HPLC have been plotted against $\delta^{13}$C$_{POC}$ (Figure 6.8). Across all algal groups there is no significant correlation with $\delta^{13}$C$_{POC}$, which prevents us from further determining the effects of individual phytoplankton groups on C isotope fractionation ($\varepsilon_p$). A limitation of this study is being able to separate and quantify the effects of a diverse number of species across the front on particular isotopic composition. South of the subtropical front, the dominant species is *Emiliania huxleyii* throughout the top 120 m, with little presence...
of other species (evidenced by an abundance of Haptophytes N which correlates with the high proportion of fnano in Figure 6.5). As this is the dominant species, it is likely the primary determinant of $\delta^{13}\text{C}_{\text{POC}}$. The dominance of a single species south of the front may be a reason for a more significant correlation between CO$_2$(aq) and $\delta^{13}\text{C}_{\text{POC}}$, as other factors may be less dominant in influencing $\epsilon_p$.

![Graphs showing correlation between δ13C_POC and chlorophyll-a for different phytoplankton species](image)

Figure 6.8 The estimated contribution of each phytoplankton species to chlorophyll-a is plotted against $\delta^{13}$C$_{\text{POC}}$. Note the different y-axis scales depending on the phytoplankton type as varying contributions were identified. No significant correlation is observed with phytoplankton group.
To test whether the observed low $\delta^{13}\text{C}_{\text{POC}}$ and high $\varepsilon_p$ on the western boundary may be the result of increased terrestrial influence, the correlation between $\delta^{13}\text{C}_{\text{POC}}$ and C:N was tested and no significant correlation was found ($r=-0.028$, $n=108$, $p=0.774$). Samples with salinities < 34 psu are influenced by the outflow of the Rio Plata. These samples consist of 5, 15 and 50 m at Station 24 and 5 m at Station 22 and deviate from the C isotope trends (Figure 6.7). To test the deviations further the relationship of $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{13}\text{C}_{\text{CO2}}$ was compared to that of $\delta^{15}\text{N}_{\text{PN}}$ and $\delta^{15}\text{N}_{\text{NO3}}$ to determine whether N isotopes give an indication of a terrestrial source. In Figure 6.9, it is clear that the Rio Plata samples fall away from reactant vs. product lines for both C and N isotopes. $\delta^{13}\text{C}_{\text{POC}}$ is lower than expected for fractionation solely from C uptake by phytoplankton and cell size data. In contrast, the N isotope data indicate a heavy N isotope source to the continental margin. These observations suggest that there may be a terrestrial source on the western boundary with land-derived low $\delta^{13}\text{C}$, high $\delta^{15}\text{N}$ and relatively low C:N. These samples are excluded from the assessment of $\varepsilon_p$, and are discussed further in Chapter 7.

In summary, $\delta^{13}\text{C}_{\text{POC}}$ variation cannot be solely explained by CO$_2$ variation as observed by high variability in $\delta^{13}\text{C}_{\text{POC}}$ across the transect. SASW samples fall closest to the expected trends using CO$_2$ variation, suggesting that other factors such as cell size/assemblages have less of an effect on $\varepsilon_p$ in this region. There is a large decoupling from expected trends in the subtropical waters. A degree of variability between $\delta^{13}\text{C}_{\text{CO2}}$ and CO$_2$ variation is observed close to the Rio Plata which suggests additional processes occurring in this region. The variation in $\varepsilon_p$ is greater than the observed CO$_2$ variation suggesting cell size is a dominant factor in determining $\varepsilon_p$ in the subtropical water masses.
Figure 6.9 $\delta^{13}C$ and $\delta^{15}N$ of reactant versus product, showing the isotopic fractionation of $N = 5\%$ and $C = 14\%$. The Rio Plata samples are indicated in grey compared to the open ocean samples. Here it is clear that for $\delta^{15}N$ the open ocean samples either fall close to the integrated product or below. The Rio Plata samples fall above the expected relationship. For $\delta^{13}C$, Rio Plato samples have isotopic signatures lower than expected for the $\delta^{13}C$ of the reactant.
6.5 Discussion

6.5.1 $\varepsilon_p$ in the SASW

Meridional transects have been used to best demonstrate the correlation between changes in CO$_2$ and $\delta^{13}$C$_{POC}$ (e.g. Rau et al., 1989), as a greater variability in CO$_2$[aq] is observed. Across 40°S there is a change in surface CO$_2$[aq] of 10.5 to 15 µmol kg$^{-1}$, with the highest concentrations evident in the lower salinity SASW. Rau et al. (1989) measured $\delta^{13}$C$_{POC}$ across a similar range of CO$_2$ concentrations, and found values of -20 to -22‰. $\delta^{13}$C$_{POC}$ is much more variable across the 40°S transect (-19 to -24‰). This suggests that latitudinal transects do not capture the zonal variability which is evident from longitudinal transect. This highlights problems with using sediment cores to look at variability in $\delta^{13}$C as one location is more likely to capture zonal variability rather than variability from CO$_2$ concentrations. Zonal variability aside from CO$_2$ concentrations may result from a greater diversity of growth rates, cell sizes and shapes of phytoplankton. Popp et al. (1998) found that the empirical relationship between $\varepsilon_p$ and $\mu$/CO$_2$ can be determined when growth rate, cell size and geometry can be constrained. Therefore CO$_2$ alone cannot be used to predict $\delta^{13}$C$_{POC}$, but other factors such as cell size and shape need to be taken into account.

The $\delta^{13}$C of phytoplankton can provide insight into the environmental conditions in which the uptake of C occurred. If a high amount of CO$_2$ is available to phytoplankton, it can lead to the preferential consumption of $^{12}$C, and the production of lighter $\delta^{13}$C$_{POC}$. This has led to its use as a proxy to construct paleo CO$_2$ concentrations (Freeman and Hayes, 1992; Jasper et al., 1994), where $\varepsilon_p$ is strongly correlated with CO$_2$[aq]. An increase in $\varepsilon_p$ with increasing CO$_2$ has been observed in a number of studies (Burkhardt et al., 1999), leading to an inverse correlation predicted between $\varepsilon_p$ and $\mu$/CO$_2$(aq). At CO$_2$ concentrations > 10 µmol kg$^{-1}$ this has been demonstrated from the diatoms *Phaeodactylum tricornutum* (Laws et al., 1995) and *Porosira glacialis* (Popp et al., 1998) and coccolithophore *Emiliania huxleyi* (Bidigare et al., 1997). Different regression lines between these species can be accounted for by variable surface area and cellular C content. In the SASW, the dominant species is *E. huxleyi* and $\delta^{13}$C$_{POC}$ correlates with both CO$_2$[aq] and cell size. I find an $\varepsilon_p$ of 12.5-14‰ which is similar to findings from a previous laboratory and
open ocean study on haptophytes (Bidigare et al., 1997). Open ocean $\varepsilon_p$ data from the Santa Monica basin and Sargasso Sea were found to correlate with PO$_4 ^{3-}$, a proxy for growth rate. Although limited by the number of samples, $\varepsilon_p$ and PO$_4 ^{3-}$ correlate strongly in the SASW (Figure 6.10). This correlation is not evident in the subtropical water masses as other factors such as cell size have a greater effect. The significant positive correlation in the SASW ($r=0.877$, $n=6$, $p=0.022$), is higher than the influence of CO$_2$[aq] ($r=0.748$, $n=6$, $p=0.087$). Higher PO$_4 ^{3-}$ concentrations give an indication of lower growth rate. In these areas higher $\varepsilon_p$ can be expressed. As cell size and species in the SASW are relatively homogeneous, these factors are less likely to influence $\varepsilon_p$, and the effects of growth rate and CO$_2$ become more distinguishable.

Figure 6.10 Relationships of $\varepsilon_p$ with PO$_4 ^{3-}$ and CO$_2$[aq]. A more significant positive correlation is observed between $\varepsilon_p$ and PO$_4 ^{3-}$ (a proxy for growth rate), suggesting that C demand within the cell is an important determinant of $\varepsilon_p$.

In the SASW, cell size does not change considerably therefore the effects of CO$_2$[aq] and growth rate in the determination of $\varepsilon_p$ can be distinguished. When phytoplankton assemblages are relatively homogeneous, the effects of cell size, membrane permeability and $\varepsilon_f$ should be fairly consistent. Therefore the fractionation related to growth rate becomes increasingly important. This does not necessarily change the
isotope effect but more the pathway of assimilation or the mechanism of C fixation. Here PO$_4^{3-}$ concentrations can be linked to growth rates and the cellular C budget. With Fe limitations on growth, higher PO$_4^{3-}$ allows higher $\epsilon_p$ as it increases carbon uptake: fixation.

The influence of cell size and CO$_2$[aq] on C isotopic fractionation ($\epsilon_p$) were compared across the transect (Figure 6.11). Modelled cell size and CO$_2$ estimates are similar for the SASW. Cell size better describes the changes in $\epsilon_p$ in the subtropical water masses. Here smaller cell sizes are identified, which best explain changes in $\epsilon_p$ (Figure 6.11). The change in $\epsilon_p$ determination highlights the decoupling between $\delta^{13}$C$_{POC}$ and temperature. It therefore appears that subtropical and subantarctic waters have different mechanisms of C fractionation, and when considering open ocean samples, cell size is a primary factor determining $\epsilon_p$ in subtropical waters.

### 6.5.3 $\epsilon_p$ in subtropical water masses

Over the full transect, a reverse trend between modelled $\epsilon_p$ and CO$_2$ is observed, an increase in $\epsilon_p$ with decreasing CO$_2$ (Figure 6.11 - indicated by the lower expected fractionation of $\epsilon_p$ in low CO$_2$ subtropical waters). This observation suggests that cell size has a greater impact on $\delta^{13}$C$_{POC}$ than CO$_2$ in subtropical water masses. If CO$_2$ rather than bicarbonate is transported into the cell, the flux will be determined by gas diffusion, and will therefore be proportional to the cell surface area. A decrease in cell radius would lead to an increase in cell surface area to volume ratio (SA:V), increasing the amount of CO$_2$ diffusing across the cell membrane and allowing greater fractionation and thus $\epsilon_p$. These cell size trends are indeed observed across the transect, with the largest cell sizes having lower $\epsilon_p$ and higher $\delta^{13}$C$_{POC}$. Smaller cell sizes may be a mechanism for phytoplankton to adapt to the low CO$_2$ in the subtropical waters and explains the abundance of picoplankton in these regions.

Factors may change $\epsilon_p$ by changing the ratio of C fixation to diffusion driven CO$_2$ uptake. If more C fixation occurs compared to specific C uptake, $\delta^{13}$C$_{POC}$ should increases and therefore lower $\epsilon_p$. This ratio can vary due to many factors, including differences in species sizes, shapes and biological mechanisms. A frontal region,
such as this study area, may increase variability in the ratio of C fixation to CO$_2$ specific C uptake and thus variability in $\delta^{13}$C$_{POC}$. In low CO$_2$ environments, increasing C uptake via increases in SA:V will increase uptake: fixation and therefore $\varepsilon_p$. In subantarctic regions, the smaller cell size is less advantageous and therefore has less of an effect on $\varepsilon_p$.

**Figure 6.11** Variation in measured and modelled $\varepsilon_p$ by longitude. Upper panel shows model variation with CO$_2$$_{[aq]}$ and the lower panel shows variation of model with changing cell size. Modelled $\varepsilon_p$ is shown with crosses. Subtropical samples are open triangles and subantarctic samples are closed circles.

A recent study found that $\varepsilon_p$ has increased significantly since the 1960s in the subtropical Atlantic, whereas no notable change has been detected in polar regions (Young et al., 2013). The variation in $\varepsilon_p$ can be explained in terms of the supply of inorganic C and its removal from biological fixation (Farquhar et al., 1982; Laws et
An increase in CO$_2$$_{aq}$, from rising atmospheric CO$_2$ concentrations, would increase the supply of inorganic C to phytoplankton. Increased CO$_2$ concentrations have led to a decrease in δ$^{13}$C$_{DIC}$ by 0.025% yr$^{-1}$ (Gruber et al., 1999), but δ$^{13}$C$_{POC}$ has decreased by 0.047 % yr$^{-1}$, suggesting $\varepsilon_p$ may also be increasing, perhaps by the increase in supply: fixation (Young et al., 2013). The sensitivity of $\varepsilon_p$ to changing CO$_2$ is determined by the CO$_2$ concentration in marine waters. Given the high concentrations in the polar regions and the upwelling of CO$_2$ rich waters at the Polar Front, further increases in CO$_2$$_{aq}$ are unlikely to have an effect on $\varepsilon_p$ as the maximum fractionation from CO$_2$ concentration is already being expressed. In contrast, in subtropical gyres, low upwelling, lower CO$_2$ and increase in C supply may be more likely to affect $\varepsilon_p$. This may be caused by the reduced use of CCMs by phytoplankton (Hopkinson et al., 2011), which is likely to have the highest effects in areas where CO$_2$ concentrations are low. Higher $\varepsilon_p$ in subtropical regions may therefore be influenced by increasing CO$_2$ concentrations, which could serve as an explanation for the greater deviation of δ$^{13}$C$_{CO2}$ and CO$_2$$_{aq}$ in Figure 6.3. In Rau et al. (1989), an observed δ$^{13}$C$_{POC}$ range of -22 to -20‰ was observed for this latitude, whereas I find a δ$^{13}$C$_{POC}$ as low as -24‰ in subtropical waters. This may further indicate that increasing CO$_2$ not only decreases δ$^{13}$C$_{CO2}$ but influences uptake mechanisms by subtropical species which may in turn increase $\varepsilon_p$.

### 6.5.4 Factors influencing $\varepsilon_p$ in different oceanic regions

As discussed, CO$_2$ is the principal determinant of δ$^{13}$C$_{POC}$ across the global ocean (Figure 6.12) (Sackett et al., 1965; Rau et al., 1989; Goeringe and Fry, 1994). CO$_2$ varies within the ocean by ~18 µM. In the colder polar regions, a higher C availability allows for greater discrimination during uptake by phytoplankton. Much more negative δ$^{13}$C$_{POC}$ excursions and higher $\varepsilon_p$ are identified in Southern Ocean phytoplankton compared to the high northern latitudes, due to the upwelling of CO$_2$ rich waters. A modelling study found that the inter-hemispheric differences in δ$^{13}$C$_{POC}$ could be explained by the inter-hemispheric asymmetry in CO$_2$ (Hofmann et al., 2000). CO$_2$ concentrations have been identified as the main factor in many observational studies (Francois et al., 1993; Jasper et al., 1994; Laws et al., 1995). With this study I show that although latitudinal transects generally capture the effect
of CO$_2$ on $\delta^{13}$C$_{POC}$, longitudinal transects demonstrate the high variability at a given latitude. Poleward of $\sim$50°S, CO$_2$ concentrations range between 15-25 µM, $\delta^{13}$C$_{POC}$ between -30 and -24‰ and $\varepsilon_p$ is greatest of anywhere in the global ocean (Figure 6.12). This is likely a region where $\varepsilon_p$ of C fixation (Rubisco) is highly expressed on $\varepsilon_p$ and other factors have less influence. The large CO$_2$ gradient south of $\sim$40°S explains the majority of $\varepsilon_p$ in $\delta^{13}$C$_{POC}$ studies from the Southern Ocean to date (Francois et al., 1993; Goericke et al., 1994). It appears that the open Southern Ocean is the most reliable marine setting for significant correlations (Figure 6.12); here there is typically low variability in species assemblages, with a dominance of diatoms (Bentaleb et al., 1998). In the Southern Ocean there is commonly a progression of diatom species over the course of the season, rather than high diversity at one given time. The lower species diversity suggests a low effect on $\varepsilon_p$ and $\delta^{13}$C$_{POC}$.

Below 15 µM CO$_2$, $\delta^{13}$C$_{POC}$ and CO$_2$ are still correlated, but with increased variability in the subtropical regions. It is clear that there is a higher degree of variability within these regions and more decoupling from the CO$_2$ concentration (6.12). In these regions, although CO$_2$ still remains high, the ratio of C fixation to CO$_2$ specific C uptake increases and thus other factors may become more important in determining $\delta^{13}$C$_{POC}$ and affect $\varepsilon_p$. In the subtropical Indian Ocean, no correlation with CO$_2$ was observed, but $\delta^{13}$C$_{POC}$ correlated well with different water masses, suggesting that each water mass carried the C isotopic signature from the local phytoplankton assemblages (Fontugne and Duplessy, 1978). Strong seasonal variations in $\delta^{13}$C$_{POC}$ are likely to be a result of changes in biological parameters such as cell radius, cell membrane permeability and growth rate (Francois et al., 1993; Goericke and Fry, 1994; Jasper et al., 1994; Laws et al., 1995; Popp et al., 1998).
Figure 6.12 Correlations of CO$_2$, δ$^{13}$C$_{CO_2}$, δ$^{13}$C$_{POC}$ and ε$_p$ with latitude. Colour indicates different studies. This study is identified in red. The range of values from this study captures the variability within one region from changes in ε$_p$.

The 40°S transect crosses the SSTC of the South Atlantic, a highly productive region. A similar study from the SSTC of the Indian Ocean (Bentaleb et al., 1998), found a decoupling between δ$^{13}$C$_{POC}$ and CO$_2$, attributed to changing physical processes across the frontal region. Both this study and that of Bentaleb et al. (1998), found δ$^{13}$C$_{POC}$ south of the front to correlate to some degree with CO$_2$, but variable water mass movements decouple this trend. A transition from the Southern Ocean to subtropical waters decreases the reliability of predicting ε$_p$ from CO$_2$ concentrations (Bentaleb et al., 1998). In addition, if water masses are converging, it is likely that
phytoplankton sampled may not have grown in that CO$_2$ regime therefore adding uncertainty in modelling $\delta^{13}$C$_{POC}$ from CO$_2$. It has been noted previously that phytoplankton assemblage-derived changes in $\varepsilon_p$ occur in the Seasonal Sea Ice Zone (SSIZ) (Dehairs et al., 1997; Popp et al., 1999) and in major frontal regions (Francois et al., 1993; Dehairs et al., 1997; Popp et al., 1999; this study). In frontal regions phytoplankton may see different CO$_2$ levels within their growth period, different nutrient regimes and hence growth rates, therefore the mixing of phytoplankton produced on either side of the front is likely to complicate any correlations. Thus it is likely that this variability will have greater effects on $\delta^{13}$C$_{POC}$ than in stable phytoplankton communities.

Subtropical environments are characterised by a high diversity of phytoplankton, therefore seem to be less correlated with CO$_2$, than phytoplankton from the Southern Ocean with a high dynamic range of CO$_2$ and relatively low diversity. Regions where frequent physical changes stimulate variable and diverse phytoplankton assemblages appear more likely to have a decoupled relationship between $\varepsilon_p$ and CO$_2$. It is therefore important to consider these effects when using $\delta^{13}$C$_{POC}$ as a palaeoproxy. Over long latitudinal transects there are less drastic changes in phytoplankton assemblages within a particular CO$_2$ range. The large change in CO$_2$ with latitude is high enough to account for a significant amount of the fractionation. This study presents a longitudinal transect which highlights the variability within one latitudinal band. This suggests that using cores from one site is likely to represent local variability principally, before it accounts for changes in CO$_2$. 
6.6 Conclusions

The stable isotopes of C are used to investigate the importance of C supply to phytoplankton growth across the frontal region of the South Atlantic. The applicability of models in determining the change in $\delta^{13}$C$_{POC}$ with changes in CO$_2$, growth rate, species and proximity to the shelf have been assessed. In this highly productive region, it is not applicable to use temperature and/or CO$_2$ concentration to determine $\delta^{13}$C$_{POC}$, with no significant correlation observed in subantarctic or subtropical waters. The SASW shows a significant correlation between $\epsilon_p$ and growth rate, as calculated using PO$_4^{3-}$ concentrations. This is attributed to lower growth rates allowing greater isotopic discrimination during uptake. It was found that cell size has an important effect on the determination of $\delta^{13}$C$_{POC}$ across the full transect, in particular in the subtropical water masses. Decreasing cell size, and thus increasing SA:V leads to higher $\epsilon_p$ and thus lower $\delta^{13}$C$_{POC}$ in the subtropical regions of the transect. The high SA:V of phytoplankton in subtropical water masses seems to be the main mechanism of increasing C uptake and allows a greater fractionation of C isotopes than is observed in the subantarctic waters. This change to higher $\epsilon_p$ north of the front suggests that species assemblages and cell size are likely to have a dominant effect on $\delta^{13}$C$_{POC}$ in subtropical regions and cannot be used to accurately determine CO$_2$[aq].
7 Sources and fate of organic matter in the South Atlantic

7.1 Abstract
Rivers and coastal regions connect the continents with the open ocean, providing a significant source of carbon and nutrients for marine productivity. Despite this, their importance in local and global carbon budgets remains unclear, mainly due to the complexity of coastal systems. A suite of isotopic measurements of organic material in suspended particles and surface sediments across the Argentine and Cape basins are used to determine the fate of organic material in the deep ocean. The organic matter in sediments across the full transect reflect marine isotopic signatures, indicating the productive surface waters are the dominant source of organic matter to the seafloor. Higher organic matter content is observed on the western slope suggesting more efficient transfer to the continental slope and abyssal sediments. This is attributed principally to the presence of the Rio Plata and Brazil Malvinas Confluence Zone which stimulates elevated phytoplankton blooms. Variability in isotopic and stoichiometric signatures in sediments across the open ocean transect can be best explained by the location of the south subtropical convergence. Subantarctic dominated waters are associated with a higher flux of organic matter to depth, higher $\delta^{15}$N, $\delta^{13}$C and lower C:N. Sediment signatures, therefore may be used to reconstruct the movement of the subtropical front over time.
7.2 Introduction

Continental shelves and slopes constitute 15-20% of ocean surface area yet these regions account for approximately 50% of ocean primary productivity and new production (Prahl et al., 1994; Eppley and Peterson, 1979). Continental margins are important for the export and transformation of organic matter from rivers to the open ocean (Hedges et al., 1997; Keil et al., 1997; Bauer et al., 2001). Through riverine input, coastal margins receive and produce an excess of organic carbon. Residual matter can be transported offshore and contribute to the productivity of the open ocean (Bauer and Druffel, 1998). Rivers are the main terrestrial source of organic matter to the coastal regions and supply ~0.9 Pg C yr$^{-1}$ to the ocean (Cole et al., 2007). Current estimates of particulate riverine input however, surpass values of total organic carbon buried in marine sediments (Raymond and Bauer, 2001). Determining the fate and relative contribution of terrestrial organic matter to the world’s oceans is imperative to the understanding of the biogeochemical cycling of carbon and nitrogen (Hedges et al., 1997). A South Atlantic transect across 40°S can evaluate the contribution of nutrients and organic matter (OM) from the South American and African continental margins. These regions likely play a part in supplying nutrients to support the high rates of productivity observed in satellite images in this region (Behrenfeld and Falkowski, 1997). Organic matter burial is relatively high close to the South West Atlantic margin and the Walvis Ridge region of the South East Atlantic (Frenz et al., 2004; Inthorn et al., 2006) and may play an important role in organic matter export from continental margins to the ocean interior.

The Rio Plata situated on the SE coast of South America at 35-36°S and 55-58°W, is sometimes regarded as a marginal sea (Nagy et al., 2002). Its drainage basin of 3.2 x10$^6$ km$^2$ is considered to be the fourth largest globally and second largest in South America following the Amazon (Panarello and Dapena, 2009; Botto et al., 2011). It is fed by numerous tributaries but the Parana River, with an average discharge of 17 300 m$^3$ s$^{-1}$, is the most dominant in terms of flow (Nagy et al., 2002). Despite its coverage, the Rio Plata’s influence on the South Atlantic margin has been little investigated. In particular, it has not yet been discerned whether the river – estuary
system provides a major source of particulate terrestrial organic matter to the coastal margin. The South West Atlantic Ocean holds an important position in global ocean circulation. Water masses are focussed to the deep western boundary under currents (Stommel, 1958) and the increased flow velocities in this region are likely to have a major impact on sedimentary processes. It has been suggested that the increased through flow in this region may cause the lateral advection of sedimentary particles (Frenz et al., 2004).

Surface currents in this region also play an important role in productivity. The north flowing Malvinas Current converges with the southwest flowing Brazil Current, close to the Rio Plata at ~38°S. This region is named the Brazil Malvinas Confluence (BMC), and the surface water masses undergo intense mixing. In addition, this region receives ~ 470 km$^3$ of fresh water and 9.2 x 10$^7$ t of sediment per year from the Rio Plata estuarine system (Milliman and Meade, 1983). The continental margin of the South West Atlantic therefore may supply terrestrial and marine organic matter to the ocean interior from the surface and via the lateral advection of particles from the shelf and slope.

In contrast to these observations, oceanographic features have less of an effect on eastern margin sedimentary processes in the southern Atlantic (Homoky et al., 2013). Discharge from rivers on the South African continent is of minor importance (Embley and Morley, 1980) and the nepheloid processes which are observed in the Walvis Ridge region are located further north than the south subtropical convergence (Inthorn et al., 2006). Core top sediments above the lysocline at ~4500 m are often high in CaCO$_3$, and on the continental slope organic carbon can be ~2% (Embley and Morley, 1980; Hensen et al., 2000). In contrast the Argentine basin sediments typically have lower CaCO$_3$ and higher organic carbon content. Sediments in the Cape Basin reflect largely high vertical organic matter flux, remineralisation and burial. The Argentine basin strong surface and bottom currents have been noted to redistribute sediments from the shelf area to the slope and basin (Klaus and Ledbetter, 1988). Our knowledge of the sedimentary processes occurring in the South Atlantic remain poorly understood. The supply of organic components to the
ocean will be investigated via investigating the fate of different sources of organic material to the shelf, slope and basin on each of these continental margins.

Isotopic signatures can be used to investigate the combination of biological and sedimentological processes which occur on each of these continental margins. Variations in $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, C:N and organic carbon content of suspended particulates and sediment cores are used to determine the cycling and fate of organic matter in the subsurface ocean. The relative contribution of marine and terrestrial derived organic matter will be determined to ascertain the transfer of organic material to the ocean floor. The contrasting continental margins provide a setting whereby the influence of river discharge, hydrographic features and sediment reworking can be explored. This transect provides a unique study of a highly productive region of open ocean combined with two contrasting continental margins. It therefore allows us to explore the relative influence of vertical carbon flux from the surface ocean and lateral flux of carbon from the continental margins. In doing so, the mechanisms which provide the most efficient transfer of carbon to the ocean floor can be determined. This is important for our understanding of the mechanisms by which terrestrial organic matter is exported from the continents to the deep sea and has implications for our understanding of the global carbon budget.
7.3 Methods

Samples were collected on board the RRS Discovery between October-November 2010 (D357) and the RRS James Cook between December 2011 and February 2012 (JC068) as part of the UKGEOTRACES 40°S transect. Particulate samples were collected onto muffle furnace (450 °C for 4h), pre weighed GF/F microfibre filters (0.7 µm pore size, 25 mm diameter). Water samples were pressure filtered simultaneously using a compressor (at ~10 psi) and an 8-way manifold system. Additional samples were collected from a towed fish at ca. 5 m depth. Once the total volume for each depth was filtered, filters were rinsed with Milli-Q water, extracted from the filter holder, placed in labelled aluminium foil and dried at 50 °C for ~12 hours. Once dried, filters were folded and placed in ziplock bags and frozen at -20 °C. Bottles and tubing were rinsed with 10% v/v HCl and then further rinsed three times with Milli-Q water between sample collections. Sediments were collected using a box mega corer. Samples were removed from the coring frame and immediately transferred to the Constant Temperature (CT) laboratory on board, which was set close to bottom water temperatures. Sediment cores were sliced in 2 cm slices; a sub sample of ~1 cm³ was taken from each 2cm slice, stored in a ziplock bag and frozen at -20 °C for δ¹³C and δ¹⁵N analysis at the University of Edinburgh. Stand Alone Pump systems (SAPS) were deployed 0.5-2 h filtering approximately 500 L seawater. The SAPS collected particles using 2 stacked 293 mm diameter pre combusted GF/F filters (0.7 µm nominal pore size). GF/F filters were recovered in a fume hood, wrapped in ashed Al foil and frozen at -70 °C.

To determine the isotopic composition of particulate organic carbon (δ¹³C_{POC}) and particulate nitrogen (δ¹⁵N_{PN}), sample filters were acidified to remove carbonates. Briefly, GF/F filters were wetted with Milli-Q and placed in a desiccator with 70% v/v HCl for 48 hours (Lourey et al., 2003). Once all the carbonates were removed, the filters were dried for 12 hours at 50 °C and folded into tin cups ready for analysis. Sediment samples were freeze-dried and homogenized using a pestle and mortar. From estimates of organic matter content, a certain weight of sample was weighed on a microbalance into silver capsules. Capsules were acidified under a clear laminar flow bench by pipetting drops of 50% HCl into the capsules. These
samples were kept on a hot plate at 50 °C and HCl added every two hours until all carbonate was removed. Capsules were then folded ready for isotopic analysis. The samples were analysed using a Carlo Erba NA 2500 elemental analyser in-line with a VG PRISM III isotope ratio mass spectrometer for elemental POC/PN and $\delta^{13}C_{POC}$ and $\delta^{15}N_{PN}$. The output of the IRMS presents raw ratios of the standards and samples. Weighed internal standards of PACs and acetanilide were run in each batch to correct for drift and absolute isotope values (See Chapter 2 for more details).
7.4 Results

The Berg and Ofilants rivers drain the South African continent slowly delivering siliciclastic material to the Cape shelf at <3 cm kyr\(^{-1}\) (Compton and Wiltshire, 2009). The upper slope of the Cape basin margin has been found to have organic carbon of approximately 1.4-2.2 wt.% and dissolved O\(_2\) is consumed within a few millimetres of the sediment water interface (Homoky et al., 2013). Although the oceanographic features of the western margin are fairly well investigated (Piola and Gordon, 1989; Stramma and England, 1999), the role and variability of the sedimentary regimes is poorly constrained. The south western continental margin sediments can be divided into coarse grained and carbonate depleted sediments to the south west and finer grained carbonate rich to the North East of the BMC (Frenz et al., 2004). Below the mixing zone of the BMC, high concentrations of organic matter and low carbonate contents have been identified in previous work (Frenz et al., 2004). Adjacent to this a clearly recognizable discharge of the Rio Plata is observed with a coarse grained tongue extending further south down the continental slope.

A basin wide difference in core top sediments is observed with lighter \(\delta^{13}C\) in the Argentine basin compared to the Cape basin (Figure 7.1). Cape basin \(\delta^{13}C_{\text{org}}\) is typically \(-19\%o\), which decreases to \(-21\%o\) in the Argentine basin. There is a peak at Station 22 of \(-20\%o\), likely a result of high productivity in surface waters transferring a heavier signature of phytoplankton to the sediments. This is mirrored in a peak in organic carbon content of \(~4\%)\, which is double the measured organic carbon content over the rest of the transect. The organic carbon content decreases from Station 22 to the abyssal plain in the Argentine basin with typical values of \(~1\)%. On the eastern margin the highest organic content is at the closest sampling location to the continental shelf, Station 0.75 of \(~2\%) organic carbon. Abyssal Cape basin sediments are slightly elevated in organic carbon at Stations 3 and 6. The \(\delta^{15}N\) mirrors these trends with lighter \(\delta^{15}N\) in the Argentine basin compared to the Cape basin, and a peak of organic nitrogen at Station 22. C:N is higher in the Argentine basin and on the eastern margin. Across the open ocean setting core top sediments therefore demonstrate a shift between higher OM content associated with heavier
$\delta^{15}N$ and $\delta^{13}C$ and lower C:N to lower OM content, lighter isotopic signatures and higher C:N.

Figure 7.1 The bathymetry of oceanic transect with sediment core locations labelled. Station numbers are the same as water sampling stations as identified in previous chapters. Associated core top trends in $\delta^{13}C$ (blue) and % organic carbon (orange), $\delta^{15}N$ (blue) and % organic nitrogen (orange) and C:N ratios are shown.

The $\delta^{13}C$ of suspended particulates in the surface 500 m typically range between -25 and -19‰ and the mechanisms which cause this variability are discussed in Chapter 6. At greater depths, lighter values are observed as low as -27‰ in the Argentine Basin and in particular on the western boundary (Figure 7.2). The lowest values are observed between 3000-4500 m on the continental slope, and in Stations 20, 21 and 22. The Argentine suspended particulates are significantly lighter in $\delta^{13}C_{POC}$ (-1‰) than the Cape basin (t-test, p = 0.003). $\delta^{15}N_{PN}$ of suspended particulates is typically
1-6‰ in the surface and intermediate waters. $\delta^{15}N_{PN}$ increases with depth throughout the transect, which may indicate increased degradation of organic matter. $\delta^{15}N_{PN}$ of particulates within ~500 m of the sediment surface are consistently between 6-7‰. Higher $\delta^{15}N_{PN}$ is also associated with the continental slope regions within close proximity to the sediment interface.

Figure 7.2 $\delta^{13}C_{POC}$, $\delta^{15}N_{PN}$ and particulate organic carbon of suspended particulates across 40°S. Lighter $\delta^{13}C_{POC}$ is identified on the western boundary of the transect with values as low as -27‰. Within 500 m of the bottom sediments, $\delta^{15}N_{PN}$ is consistently ~7‰. POC is elevated in surface waters but rapidly decreases from 100-200 m depth. Higher POC concentrations are observed close to the Mid Atlantic Ridge and the western slope boundary.
The concentration of particulate organic carbon (POC) is typically between 1-2 µmol L⁻¹ in the surface waters and rapidly decreases between 100-200 m. Below the thermocline, suspended POC is less than 0.2 µmol L⁻¹ through both basins with elevated concentrations at the Mid Atlantic Ridge (up to 0.3 µmol L⁻¹) and the western continental slope boundary (up to 0.2 µmol L⁻¹). The elevated POC concentrations at the Mid Atlantic Ridge are likely from resuspension processes and interaction between the bathymetry and bottom currents. Profiles of suspended particulates in the Argentine basin typically have decreasing δ¹³C_POC with depth, in particular in bottom samples of each profile and stations close to the western boundary (Figure 7.3). The low δ¹³C_POC samples are associated with higher δ¹⁵N_PN and C:N ratios compared to samples from higher in the water column and further from the continental slope.

Figure 7.3 Profiles of δ¹³C, δ¹⁵N and C:N of suspended particulates from the western boundary. Samples within the black dashed lines represent low δ¹³C associated with the western continental slope. The low δ¹³C samples correspond with high δ¹⁵N and C:N.

The δ¹³C of organic matter in sediments in an open ocean setting should largely represent the sinking organic matter flux. In this study, sediment δ¹³C ranges between -19 and -22‰, which is ~2-3‰ heavier than suspended particles (Figure 7.4). This likely shows a significant difference between sinking and suspended
particles. Although there is a similar range for both the Cape and the Argentine sediment samples, cores are consistently heavier in the Cape basin in comparison to the Argentine basin and there is a highly significant difference between bulk δ¹³C in the western and eastern basins (t-test, p=<0.001). A mean value of -20.4‰ is observed for the Argentine basin and -19.3‰ for the Cape basin. Two cores (Stations 24 and 3), show large excursions with depth. Station 24 has surface values of ~-20.5‰, which below 8 cm depth increase in δ¹³C with the heaviest evident at ~15 cm depth. Station 3 shows the opposite excursion with heavier values at the surface of ~-19‰ which decrease in δ¹³C with depth. The δ¹⁵N from the western basin is relatively homogeneous with samples ranging between 6.5‰ and 7.5‰. These fall within the range of suspended particulates close to the sediment surface in the Argentine basin which suggests that there is little diagenesis from the water column to sediments. There is more variability in the eastern basin in δ¹⁵N with a range in the cores of from 5 to 8.5‰ although no trend with proximity to the continental margin is observed. The large range in sediment C and N isotope signatures suggests dynamic changes in the transfer of organic material to sediments.

Station 22, located on the continental slope, has markedly higher organic content than the rest of the transect with >4 wt.% organic carbon (Figure 7.5). Station 24 which is the closest to the western boundary was observed to have coarser, sandy sediments, suggesting that the organic carbon is transported further offshore, rather than deposited in this region. From Station 22 offshore, the organic carbon content decreases to ~1%. On the eastern margin, the highest wt.% carbon and the second highest across the transect is Station 0.75, with ~2.5 wt.% carbon. Cape basin sediments have organic matter C content of 0.75-1%. In Figure 7.6, the correlations of δ¹³C with δ¹⁵N, C:N and organic carbon are investigated. There is a highly significant positive correlation between δ¹³C and δ¹⁵N in the sediments (r=0.65, n=96, p=<0.001) with lighter δ¹³C and lighter δ¹⁵N in the Argentine basin. There is no significant correlation between δ¹³C and C:N or organic carbon in the sediments (Figure 7.6). The large dynamic range in δ¹³C and δ¹⁵N is also evident in surface suspended particles as demonstrated in Figure 7.7. These differences in sediment properties and suspended sediments will be explored further in the discussion. The
δ¹³C in Argentine sediments is lighter than the Cape basin and there is a tendency towards higher C:N ratios (Figure 7.6). These results suggest that the supply of organic matter to sediments across the transect is largely from phytoplankton derived material from the surface ocean. The large range in sediment signatures suggest the supply of material to sediments is variable and the reasons for these changes will be discussed below.

Figure 7.4 A comparison between the δ¹³C of suspended particles from the CTD, SAP deployments and bottom sediments. There is an observed increase in δ¹³C of ~4‰ in bottom sediments compared to suspended particles, suggesting that vertical sinking flux is heavier than the particles analysed here, or that there has been a recent change in the isotopic signature.
Figure 7.5 Sediment core profiles of % wt.% organic carbon, $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$. Closed circles represent the Cape basin and open circles represent the Argentine basin, core locations are shown in Figure 7.1.
Figure 7.6 Sediment $\delta^{13}C_{org}$ data plotted against $\delta^{15}N_{org}$, % organic carbon and C:N ratio. Cape basin stations are represented with closed circles and Argentine basin samples are represented with open circles.
7.6 Discussion

In this section the supply of organic matter to the deep ocean will be discussed. Firstly, this will be undertaken by investigating the influence of terrestrial organic matter to the shelf and slope regions. Secondly, the dominance of marine derived organic matter in sediments will be discussed, and the reasons for variability in isotopic signatures observed.

7.6.1 Terrestrial Influence from the shelf

In surface waters $\delta^{13}\text{C}_{\text{POC}}$ variability can be largely explained by carbon isotope fractionation in the uptake of dissolved $\text{CO}_2$ by phytoplankton (Chapter 6). Surface samples from the low salinity waters close the Rio Plata, however decouple from these trends (See Chapter 6). The bulk parameters of C:N and $\delta^{15}\text{N}$ in combination with $\delta^{13}\text{C}$ can be used to investigate allochthorous sources of organic matter to a coastal boundary. There is a difference in total carbon and nitrogen values between marine and terrestrial sources which allows the relative sources to be assessed. Cellulose present in terrestrial plants, results in a higher C:N of $>$ 20 and higher protein content in marine organisms results in lower C:N of 5-8. Degradation of terrestrial organic matter can lower C:N. Therefore soil has lower values than cellulose detritus (~8-9). Organic matter sources can be examined further using $\delta^{15}\text{N}$. Terrestrial plants obtain their nitrogen indirectly through soil that fixes atmospheric $\text{N}_2$ with a $\delta^{15}\text{N}$ signature of 0‰ typically leading to lighter $\delta^{15}\text{N}$ than marine sources. In contrast, N processing within soil and aquatic systems and anthropogenic sources via wastewater may cause $\delta^{15}\text{N}$ enrichment in residual organic matter.

$\delta^{15}\text{N}_{\text{PN}}$ is enriched in comparison to $\delta^{15}\text{N}_{\text{NO}_3}$ close to the western boundary, which suggests a source of heavier $\delta^{15}\text{N}$ to the region (Chapter 6). In contrast the $\delta^{13}\text{C}_{\text{CO}_2}$ is high, yet the measured $\delta^{13}\text{C}_{\text{POC}}$ is low suggesting either a lower $\delta^{13}\text{C}_{\text{POC}}$ source or a source of high $\delta^{13}\text{C}_{\text{CO}_2}$. C:N ratios are very close to marine values (5–7) suggesting a dominance of phytoplankton. These parameters suggest a terrestrial source of organic matter to the western boundary which has low $\delta^{13}\text{C}$, high $\delta^{15}\text{N}$ and relatively low C:N. Particulate organic matter in estuaries is a mixture of terrestrial and marine components, which consist of phytoplankton, organic detritus and eroded material.
from soils and sediments. The Rio Plata is one of the largest estuarine systems in South America and processes within this system are likely to impact the isotopic and stoichiometric properties of organic matter. In addition there is extensive industrial development and urbanisation from large cities such as Buenos Aires and Montevideo. The catchment consists of C₄ salt marshes, with *Spartina* sp. covering ~32,000 ha of land on the margin of the terrestrial - aquatic environment and C₃ freshwater marshes such as *Schenoplectus californicus* (Botto et al., 2011). The presence of both C₃ and C₄ species in the estuarine system suggests there may be a wide range of δ¹³C sources that contribute to this region.

A recent study observed the isotopic and stoichiometric characteristics of C and N in the Rio Plata estuary (Botto et al., 2011). Close to the Maximum Turbidity Zone (MTZ), low light availability limits phytoplankton growth (Acha et al., 2008), but immediately offshore they quickly dominate the system. A high variability of δ¹³C in the Rio Plata estuary is measured with different plant species (Figure 7.7): with C₃ marsh plants ranging between -25 and -28‰ and C₄ *Spartina* at ~ -13‰. Particulate organic matter in the MTZ ranged between -22 and -18‰ for δ¹³C and was relatively enriched in δ¹⁵N. δ¹³C values were found to be similar to phytoplankton and C:N was ~8.5, further indicating that the organic matter is supplied principally from phytoplankton and a small amount of organic detritus. The high δ¹⁵N values suggest an influence of nutrients from the surrounding anthropogenic sources, especially wastewater or processing within the estuarine system (Acha et al., 2003). Macro detritus from the same zone showed δ¹³C of ~ -23‰ and C:N of 10.5, and detritus of long fibres suggesting a dominance of terrestrial C₃ plants from freshwater marshes. These lower C:N values for observed macro detritus of 10.5 suggests that the OM is highly decomposed.

As the C:N ratios from the MTZ are lower than expected for terrestrial origin, organic matter supplied to the shelf from the estuary is likely to be principally from highly degraded organic matter, which has lower C:N. δ¹⁵N is high in the MTZ and is supported by high δ¹⁵N of particulate N and nitrate in the shelf region. There may be a variety of causes for high δ¹⁵N. This is a highly urbanised estuarine system therefore wastewater treatment may cause the removal of N in hypoxic conditions.
and lead to an increase in δ\(^{15}\)N. The outflow of the Rio Plata is characterised by low nitrate and high phosphate concentrations (see Chapter 3). This may provide reasoning for denitrification processes within the estuarine system leading to heavier δ\(^{15}\)N supplied to the shelf region. The influence of the Rio Plata therefore appears to be best indicated by the enriched δ\(^{15}\)N identified at Station 24 and at 5 m in Station 22. However it is observed that phytoplankton are the dominant source of organic material within the water column, even close to the western boundary. The BMC likely reduces the effects of allochthonous material as the high nutrient region fuels high standing stocks of phytoplankton. The high δ\(^{15}\)N of the Rio Plata rapidly changes to low δ\(^{15}\)N within the Brazil Current, as the subtropical water mass dominates (Figure 7.7).

Figure 7.7 δ\(^{13}\)C vs. δ\(^{15}\)N of the western boundary samples. The samples with the lowest salinities (Station 24) fall closer to the measured POM values of the Rio Plata from Botto et al., 2011. The blue and green points represent the mean values measured in the MTZ (Maximum turbidity Zone) and in macrodetritus from Botto et al., 2011, error bars represent the range of values measured (2σ). The two 5 m samples from St 22 and 24 have a measured δ\(^{15}\)N \(_{PN}\) of >8‰.
7.6.2 Terrestrial influence from the western slope

Terrigenous sediments are supplied to the Argentine basin from the South American continent from high river discharge and erosion (Frenz et al., 2004; Milliman and Meade, 1983). Detritus has also been discussed to be added from the Antarctic continent by the Antarctic Bottom Water (AABW), and has been suggested to be the primary sediment supply to the basin (Conte et al., 2006). Large loads of sediments are transported as suspended particulate matter in a ~1km thick nepheloid layer within the abyssal plain of the Argentine basin (Biscaye and Eittreim, 1977). The composition and distribution of sediment in the western basin is controlled by both gravity controlled mass flows and lateral transport of sediments via bottom boundary currents (Petschick et al., 1996; Hensen et al., 2000). At intermediate depths, sediment distribution is linked to the transit of the deep western boundary current attached to the western margin. Circulation features are thought to enhance the transport of particles to the Argentine basin within this region (Niemann, 2003). The light δ^{13}C of deep suspended particulates which dominates the subsurface on the western boundary is not consistent with a downward trend of OM through the water column, but seems to signify lateral transport. δ^{13}C of suspended particles do not generally show a shift with diagenetic effects as there is minimal fractionation in δ^{13}C with breakdown of particles (Freeman, 2001). This would suggest the δ^{13}C excursion may result from the lateral transport of suspended particulates with a distinct origin to surface ocean δ^{13}C. These samples correspond with higher C:N and higher δ^{15}N which may suggest aged and degraded terrestrial material (Figure 7.3).

The influence of the Rio Plata reaches far out into the continental slope as has been evidenced by the size fractions of sediments (Frenz et al., 2004). In higher energy environments fine grained low density particles are more likely to be re-suspended and incorporated into nepheloid aggregates. Higher density organic matter aggregates may remain incorporated into sediments on the seafloor in comparison to lighter fractions which could interact with lithogenic particles. Evidence has previously been noted for the lateral transport of lithogenic derived particles and associated POC on continental margins (Sherrell et al., 1998; Hung et al., 1999). These studies suggest that seaward input of old terrestrial derived material may be significant from continental slopes to the deep ocean. Light δ^{13}C_{DOC} and suspended
POC enriched in lignin have been found in the deep ocean highlighting an input of terrestrial organic matter to the open ocean by sediment processes within the shelf and slope regions (Benner et al., 1997).

Slope failure, seafloor cracking and erosion of submarine canyon walls are all mechanisms by which aged and potentially light $\delta^{13}$C may be added to slope regions. If lateral transport of terrestrial derived organic matter through a nepheloid layer or slope transport processes causing these observations, POC and PN would likely show an elevation, characteristic of nepheloid layers (Guo and Santschi, 2000). Elevated POC concentrations are observed on the slope and in the bottom waters of the Argentine basin on the western margin (Figure 7.2). Particulate aluminium (Al) is associated with refractory aluminosilicates and can also influence organic matter cycling within slope regions (Orians and Bruland, 1986). Al enrichments are observed close to the western boundary slope which may suggest deep sediment re-suspension or horizontal advection of particles from the slope region of the western boundary (Figure 7.8). Particulate Al concentrations are highest in the bottom waters of the transect, below ~4000 m with Al concentrations reaching as high as 600 nM. Low POC/Al ratios demonstrate a lithogenic source of organic matter compared to sinking surface derived organics with high POC/Al ratios (Figure 7.8). Low POC/Al are identified on the western slope and deep basin of the Argentine basin and to a lesser degree on the eastern slope. The higher Al concentrations are associated with lighter $\delta^{13}$C of suspended particulates (apart from the Rio Plata sample identified in Figure 7.8).
Figure 7.8 a. POC/Al ratios on both continental margins, the lowest POC/Al ratios are identified on the Argentine slope and within the Antarctic Bottom Water. b. $\delta^{13}C_{POC}$ vs. log (Al) concentration. The lowest $\delta^{13}C$ and highest Al are associated with the western boundary. Very high Al is associated with the Rio Plata, with $\delta^{13}C$ of -22‰, however samples with high Al associated with the slope have lower $\delta^{13}C$ (-27 to -25‰).

The existence of a deep nepheloid layer in the Argentine basin has been noted in previous work (e.g. Hensen et al., 2000, Conte et al., 2006). Organic rich particle loads have been described within the nepheloid layer which is located in the bottom waters (Richardson et al., 1993). The importance of the nepheloid layer in this region has been hypothesised to be in part from the strong western boundary currents on the continental margin. Evidence has been given for the long distance transport of diatoms from the Southern Ocean within the Argentine basin (Jones and Johnson, 1984). In these bottom waters $\delta^{13}C$ is heavier than the western slope values, which may suggest organic matter within the nepheloid layer has a distinct source (Figure 7.2). The organic material is likely an accumulation of material from the surface...
ocean, transport from the Antarctic regions via the AABW and also from episodic slope processes. This may be further explored through the use of specific biomarkers.

In contrast to the bottom waters, the slope region has lower $\delta^{13}$C and is associated with high clay content (Figure 7.9). Admixing of the North Atlantic Deep Water (NADW) and Circumpolar Deep Water is indicated by increasing kaolinite and decreasing chlorite concentration (Petschick et al., 1996). $^{231}$Pa$_{ex}$/$^{230}$Th$_{ex}$ measurements in sediments at intermediate depths on the western boundary are low which may be linked to the fast flowing NADW which is believed to enhance particle transport to this region (Niemann, 2003). A high amount of clay particles are observed on the western margin and may complement the association of terrestrial organic matter with clay minerals and lighter $\delta^{13}$C in this region (Figure 7.9). Organic matter that is derived from terrestrial origins may include a significant amount of biologically resistant compounds such as lignin and kerogen and may also contain organic matter already strongly degraded by microbes (Bergamaschi et al., 1997). Terrestrial derived organic matter can have a higher preservation potential in sediment interactions than marine derived organic matter (Mollenhauer and Eglinton, 2007). This may indicate an aged organic matter component associated with clays on the western slope that is in part terrestrial-derived.

It has been suggested that suspended particulates within the deep ocean consist of a source of relatively young carbon derived from phytoplankton within the surface ocean and an older source of carbon. Lower $\Delta^{14}$C has been observed in suspended sediments in comparison to sinking particles (Hwang et al., 2010). A study of the Mid Atlantic Bight found isotopically light $\delta^{13}$C$_{POC}$ in deep slope waters of 31.6 to 25.6‰, which is within a similar range to the isotopically light $\delta^{13}$C on the western margin of the Argentine basin (Bauer et al., 2002). Using $\Delta^{14}$C constraints, they found older particles to have lower $\delta^{13}$C and while shelf and shallow slope samples were young, deeper slope sediments were old and had depleted in $\delta^{13}$C. The sources may be further constrained with $\Delta^{14}$C measurements which will be carried out on samples from this transect in the near future (Maria Hernandez-Sanchez, personal communication).
Figure 7.9 Features of the western margin. Here high clay content is observed within the region of low $\delta^{13}$C on the western margin (taken from Neumann, 2003)

At present our data cannot constrain the mechanisms for the variation in deep suspended $\delta^{13}\text{C}_{\text{POC}}$ compared to surface samples. Further samples need to be analysed to assess whether the high Al concentrations in the slope and bottom waters are associated with light $\delta^{13}\text{C}_{\text{POC}}$ and slight changes in $\delta^{15}\text{N}$ and C:N. The low $\delta^{13}$C signal from the slope suggests an aged or degraded terrestrial source or perhaps interaction with the dissolved pool. High river discharge on the western boundary, may supply low $\delta^{13}$C to deep suspended particulates in this slope region. It appears that the principal mechanism of terrestrial organic matter transport to the deep ocean in this region is via lateral transport from the slope rather than the downward sinking of particles which is dominated by phytoplankton signatures. As the lighter $\delta^{13}$C is not observed in the sediments or the suspended surface particulates, I suggest that the contribution from the western slope region to sediments is low. A winnowing effect has been suggested on the western slope responsible for contourite deposits and a complex system of turbidity channels has been observed (Frenz et al., 2004). These features suggest that there is interaction between the slope and western boundary currents. The clays are likely to be remobilized and these have greater associations
with terrestrial organic carbon, thus providing a possible mechanism for lighter $\delta^{13}C$ signatures on the western boundary slope. From this work, it appears that the continental margins do not supply a significant amount of organic matter to sediments in this region; instead the vertical flux from surface waters is more dominant. Although no terrestrial influence is evidenced in the sediments, the lighter $\delta^{13}C$ in suspended particulates suggest that slope processes may provide a lateral source of terrestrial derived C to the water column.

7.6.3 Transfer of organic matter to sediments

Particulate organic matter within the deep ocean is separated into suspended and sinking particles. Sediment organic matter in the open ocean should largely represent the sinking organic matter flux from the surface ocean. In this section the extent at which organic matter is effectively supplied to the sediments from the surface ocean is discussed. Primary production is high throughout the south subtropical convergence, a result of the meeting of contrasting nutrient regimes (Browning et al., 2014). Estimates from satellite images suggest $\sim$75-400 g C m$^{-2}$ yr$^{-1}$ is produced in the surface waters of this convergence region with higher rates of approximately 450 g C m$^{-2}$ yr$^{-1}$ produced on the western shelf region and within the BMC (Behrenfeld and Falkowski, 1997). These high primary production rates suggest a significant organic matter flux from the surface ocean, in particular to the shelf and slope regions.

The distribution of organic matter content within sediments of the western margin follows the observations of Frenz et al. (2004). At Station 24 which is located on the shelf, coarse grained sediments are identified with low organic content. Here a high energy environment transports particulate matter further offshore. Slightly higher organic matter is observed in core top sediments at Station 23. The highest organic carbon content is measured at Station 22, located on the continental slope, corresponding to the region of organic matter focussing (located at 53°W), allowing a higher sedimentation of organic matter flux from the surface ocean. Rio Plata nutrients are exported from the shelf with high Fe and P concentrations (See Chapter 3, Section 3.4.5); at the BMC they meet with the Malvinas and Brazil currents.
creating a complex region of eddies and surface currents. This creates a highly productive region, which is also considered to increase the vertical flux of organic matter out of the surface layer (Frenz et al., 2004). Surface currents are transported off the shelf, lose energy with increasing water depth and increase the vertical flux of organic particles to the slope. This feature which is unique to the BMC region may explain the substantially higher organic content on the western margin, suggesting that the BMC plays a large role in the effective transfer of organic matter to the deep ocean.

The high organic matter flux is derived from marine phytoplankton in the surface waters, with δ^{13}C in sediments ranging between -22 and -19‰. Sediments are typically more enriched in δ^{13}C compared to the surface suspended particulates (-25 and -19‰) across the two basins (Figure 7.3). This suggests that the vertical sinking flux of organic matter supplied to sediments is heavier than the surface phytoplankton sampled at this time. This could be caused by variability in the particles produced in surface waters over the course of the season or that there has been a recent shift towards lighter δ^{13}C production by phytoplankton at the surface. The surface suspended particles can give an indication of the expected isotopic range which will contribute to the vertical sinking flux, however are likely to be more variable. In contrast, sediments will produce an integrated signal over thousands of years. Lower δ^{13}C in surface waters compared to sediments have been described in previous work. A shift to lighter δ^{13}C in surface plankton has been identified in the South Atlantic (Fischer et al., 1998). It has been observed that the sinking δ^{13}C is lighter than δ^{13}C in sediments by ~2‰ in the subtropical Atlantic and by 3 to 4.6‰ in the Southern Ocean. At 40°S sediments measured were typically -22‰ and a high variability in surface phytoplankton of -28 to -20‰ was observed, comparable to this study (Fischer et al., 1998). These differences were attributed to increases in CO₂ availability in surface waters, and lighter δ^{13}C_CO₂ causing decreases in δ^{13}C_POC. Assuming a sedimentation rate of 1-5 cm kyr⁻¹, organic matter in surface sediments should represent phytoplankton produced with preindustrial concentrations of CO₂ in the surface waters. One explanation therefore may be that increasing anthropogenic
CO₂ concentrations are causing discrepancies between particles formed in the surface layer and the underlying sediments.

There is however a large dynamic range in δ¹³C and δ¹⁵N in sediment cores across the transect (Figure 7.6); suggesting variability in the vertical flux of particles in this region over time. Lighter δ¹³C in surface waters of this transect is typically associated with smaller phytoplankton and subtropical waters (Chapter 6). Subtropical waters also have lighter δ¹⁵N as a result of a contribution from N₂ fixers (Chapter 3), although this is slightly complicated by Rayleigh fractionation producing light δ¹⁵N in high nitrate waters. In general, across this transect subtropical particles are typically lighter in δ¹³C and δ¹⁵N than the subantarctic regions. This may suggest that there is a dominance of larger phytoplankton/subantarctic sourced organic material exported from the surface layer and propagated to depth. This is intuitive, as larger particles are more likely to be exported from the surface layer due to greater density. Additionally, the observed low recycling efficiency in Chapter 3 would suggest a greater export of organic matter from the subantarctic compared to the subtropics where macronutrients are rapidly recycled. As this is a frontal region, the importance of different phytoplankton assemblages and the isotopic signatures associated may change depending on the average position of the front. Over the course of organic sediment build up, any frontal changes may become significant.
Sources and fate of organic matter in the deep ocean

Figure 7.10 Correlations between δ¹⁵N and δ¹³C across the sediment cores and surface particulates. Cape and Argentine sediments are represent with Red squares ($r^2 = 0.57$) and blue diamonds ($r^2 = 0.45$) respectively. This suggests that there has been a shift between lighter δ¹⁵N and δ¹³C to heavier δ¹⁵N and δ¹³C. This trend is somewhat shown in the suspended particulates, although with greater variability. Suspended particulates are typically lighter than the sediments, which may represent a higher dominance of subtropical samples. An $r^2$ of 0.7 is observed when using all samples.

As has been noted there is a trend from low δ¹³C and δ¹⁵N to high δ¹³C and δ¹⁵N in the sediment cores ($r=0.65$, n=96, p<0.001). There is a similar correlation between these parameters in suspended particles in the surface 40 m (Figure 7.10). Suspended particles fall towards the lower end of this trend, suggesting that either the suspended particles sampled represent a more subtropical dominated source or that there has been a transition to lower values. Either of these processes may occur. As the sampling took place towards the end of the season, it is likely that the surface samples at 40°S have a bias towards subtropical derived OM. In addition, diagenetic processes may lead to slightly higher δ¹⁵N in the sediments compared to the surface particulates. This variability in sediment cores is also observed in the core top sediments (Figure 7.1), with shifts from high δ¹³C and δ¹⁵N to low δ¹³C and δ¹⁵N. These trends to higher δ¹³C and δ¹⁵N are associated with increases in OM content and lower C:N. Core top sediments are less likely to have undergone diagenetic
processes or be affected by differences in deposition rates compared to down-core sediments therefore may give the best estimate of the influence of the front. The higher OM content may result from a greater propagation of subantarctic derived material to the sediments. Throughout this dissertation distinct regimes have been noted north and south of the front. In the subantarctic waters, low biological demand for N and a low diversity in phytoplankton species is identified. In contrast north of the front in subtropical water masses, a higher diversity of phytoplankton and high recycling of nutrients has been observed. The smaller cell sizes lead to higher carbon isotope fractionation in these regions. The subtropical front moves seasonally, and its average latitude is likely to change with distinct climate regimes over sediment deposition timescales. The variability in open ocean C and N signatures in OM suggest that the location of the front determines the supply of OM to sediments.

In surface waters the overriding signature is of marine derived organic matter, and this signal is propagated to the sediments. The vertical flux of organic matter is more significant than terrestrial sources in this region. Light $\delta^{13}$C captured in the suspended sediments suggest that there are important sedimentary processes occurring in the western slope region and that lithogenic particles may have a significant role in complexing with organic particles. However the basin-scale differences in $\delta^{13}$C, $\delta^{15}$N and C:N in sediments appears to be largely derived from the location of the front. The highest organic matter content in sediments across this transect is observed on the western slope, fuelled by nutrient supply from the mixing of biogeochemical regimes at the BMC. On both boundaries the highest organic matter is evidenced on the slope regions. The higher organic matter burial on the western margin likely results from the Rio Plata river system providing a more effective transfer of organic matter, and additional nutrients that result in enhanced productivity. I find evidence for the position of the front in determining particle composition which is exported to depth. It appears the subantarctic waters have a tendency to higher $\delta^{15}$N, $\delta^{13}$C and lower C:N than the subtropical waters and also a higher OM content. Therefore the movement of the front appears to have an effect on the amount of organic material propagated to depth in these basins, with the subantarctic regime more effectively transferring particles to depth.
7.7 Conclusions

Organic matter supplied to sediments across this transect are predominantly sourced from a sinking vertical flux of marine-derived material. Lighter $\delta^{13}C$ observed in the western Argentine basin suspended particulates are associated with higher Al content suggesting the presence of a suspended nepheloid layer on the continental slope. The light $\delta^{13}C$ signatures within suspended particulates may be associated with aged carbon that has a high proportion of terrestrial derived matter. This is supported by low $\delta^{15}N$ and higher C:N values. This lateral transport may be encouraged through its incorporation into aluminium based organic complexation reactions. It is found that the BMC plays an important role in the transfer of a high organic matter flux to sediments on the western margin of the Argentine basin. Although principally marine derived, the interplay of the Rio Plata outflow with the Brazil and Malvinas currents provides nutrients for sustaining elevated biomass in surface waters. Core top sediments provide evidence for two contrasting sources of vertically supplied organic matter. Variability in $\delta^{13}C$ and $\delta^{15}N$ may be caused by the position of the subtropical front and the relative proportion of subantarctic and subtropical derived particles. A comparison of particulates in the surface layer shows an observable trend between low $\delta^{13}C$ and $\delta^{15}N$ subtropical particulates and high $\delta^{13}C$ and $\delta^{15}N$ in subantarctic derived material. Observations in core top sediments suggest a dominance of subantarctic derived material in the Cape basin, associated with higher organic carbon and lower C:N. The Western basin appears to be more dominated by subtropical derived particulates although this region may also be affected by the Rio Plata from the higher observed C:N ratios.
8 Conclusions

The results of this study have provided a comprehensive assessment of N and C cycling in the South Atlantic and have alluded to varying biogeochemical processes which determine marine productivity in this region.

8.1 N Cycling in the South Atlantic

8.1.1 N cycling in the subantarctic and subtropics

An in-depth comparison has been made between surface N cycling processes in the subantarctic and the subtropics. In the subantarctic, high concentrations of nitrate are transported laterally from the Southern Ocean and Fe limitation decreases biological demand for N (Figure 8.1). In the surface layer nitrate dynamics can be described by Rayleigh fractionation. An isotope effect of 5‰ is found for the algal consumption of nitrate, which is similar to most regions of the Southern Ocean. Dual isotope signatures allow further investigation into the nitrate recycling. Lower δ¹⁵N(NO₃) compared to δ¹⁸O(NO₃) is identified at the base of the mixed layer of the subantarctic waters. This is attributed to high ammonium concentrations and fractionation during the process of ammonium oxidation. In these waters, the build-up of ammonium results from high macronutrients and low micronutrient availability leading to reduced N uptake.

Figure 8.1 An overview of the nutrient cycling processes in the subantarctic and subtropical water masses. The supply of fixed N in the subtropics determines the extent of primary production. In these regions, the extent of input from diazotrophs, atmospheric deposition or subsurface supply is likely to directly impact primary production.
In the subtropical water masses, nitrate concentrations are low and limit production. Here recycling processes become dominant in supplying nutrients to the mixed layer. N\(_2\) fixers provide a significant source of new N in all subtropical water masses at 40\(^\circ\)S. Newly fixed N supports 30-50% of production in the South Atlantic Central water and Agulhas Current. This finding corroborates the importance of diazotroph abundance to primary production in subtropical gyres where fixed N limits production. Up to 75% of export production in the Brazil Current is supplied by newly fixed N. This high estimate indicates that diazotrophs may be present in the SW Atlantic and supply a significant source of new N to the Atlantic basin. Recent work identifying H\(_2\) saturations in this region support this claim (Moore et al., 2014). Atmospheric deposition is estimated to supply <10% of fixed N across the transect, having a low influence on productivity compared to diazotroph input. The effects of atmospheric deposition are likely to increase in the northern subtropical gyres as continental land mass increases.

### 8.1.2 Low latitude productivity

The intermediate waters which form in the subantarctic supply nutrients to the low latitude ocean (Sarmiento et al., 2004). Their nitrate isotope characteristics are comparable in the Atlantic, Indian and Pacific basins suggesting similar formation processes throughout the subantarctic. The modification of these water masses through the low latitude Atlantic has been investigated. Nitrate supplied in these isopycnals is quickly consumed by phytoplankton, as fixed N is the primary limitation on low latitude production. Preformed nitrate is converted to recycled nitrate above a density of ~27 kg m\(^{-3}\) (the low latitude pycnocline), as evidenced by decreases in \(\delta^{18}O_{NO_3}\). As these water masses typically have excess P in comparison to N (Moore et al., 2009, Straub et al., 2013), it provides a means by which diazotrophs can proliferate in the low latitude ocean. In the subtropical Atlantic, approximately 15% of nitrate throughout this density range is of N\(_2\) fixation origin, constituting 26-36 Tg N yr\(^{-1}\). This estimate identifies the Atlantic basin as a source of new N to the global ocean. Fe deposition and high P recycling efficiency may lead to greater N\(_2\) fixation rates than can be explained by the supply of excess P to the Atlantic basin. This work highlights the importance of disentangling the influences
of atmospheric deposition and N\textsubscript{2} fixation to further determine the mechanisms which control new N input to this basin.

8.1.3 Feedbacks within the marine N cycle

The isotopic signatures of remineralised nitrate added to the ocean interior are assessed. In doing so, the amount of low δ\textsuperscript{15}N required to balance δ\textsuperscript{15}N enrichment via pelagic denitrification is quantified. N loss in each basin is counteracted by a similar degree of diazotroph abundance which prevents any significant loss of N to the global ocean. Using this approach, N\textsubscript{2} fixation rates of 92-116 Tg N yr\textsuperscript{-1} in the Pacific and 24-32 Tg N yr\textsuperscript{-1} in the Indian Ocean are estimated. Combining Atlantic N\textsubscript{2} fixation rates of 26-36 Tg N yr\textsuperscript{-1} with Indo-Pacific rates, a global marine N\textsubscript{2} fixation rate of 142-184 Tg N yr\textsuperscript{-1} is estimated. This balances the most recent estimates of denitrification and suggests that the two principal processes which perturb the marine N cycle are relatively balanced within the marine system. The Atlantic remains a region where the processes may be decoupled but this remains a small proportion of global N\textsubscript{2} fixation. The excess N supplied to the Atlantic basin may balance loss of N from the Southern Ocean. N\textsubscript{2} fixation rates within each basin are largely determined by the supply of P and thus provide a mechanism by which the N cycle has remained relatively stable over the last several thousand years.

8.2 Carbon uptake and addition to the ocean interior

8.2.1 C cycling in the subantarctic and subtropics

The variability of primary production in the subantarctic and subtropics is further determined by investigating the uptake processes by phytoplankton in surface waters. The principal mechanisms of C isotope fractionation vary across the front. In the subantarctic, high concentrations of CO\textsubscript{2}[aq] and a lower demand for macronutrients, lead to C fractionation principally determined by growth rate and CO\textsubscript{2}[aq]. Lower δ\textsuperscript{13}C\textsubscript{POC} is identified in the subtropical waters in contrast to the expected trends of CO\textsubscript{2}[aq] determining δ\textsuperscript{13}C\textsubscript{POC} and argue against its use as a palaeoproxy. Instead it is found that cell size is the principal mechanism for increasing uptake of CO\textsubscript{2}[aq]. Carbon concentrating mechanisms are usually more common in subtropical waters as a way of increasing C uptake by utilising bicarbonate. Here I find no evidence for
these mechanisms, with $\delta^{13}C_{\text{POC}}$ consistently lower than would be expected from CO$_2$[aq].

8.2.2 Supply of organic matter to the ocean interior

Across the full transect, marine-derived organic carbon is the principal supply of material to sediments, even in close proximity to the Rio Plata region. This finding highlights the importance of phytoplankton blooms in this productive region. High organic carbon was found in sediments on the western boundary as a result of increased primary productivity at the Brazil Malvinas Confluence. The different mechanisms of uptake and supply in phytoplankton across the two biogeochemical regimes produce variable composition of exported organic material. Changes in sediment composition across the open ocean transect are explained by frontal movements and shifts between subantarctic and subtropical regimes. The subantarctic regime is characterised by higher organic material and heavy carbon and nitrogen isotope signatures. This finding suggests that under subantarctic regimes there is a greater transfer of organic matter to the sediments; supported by higher density of phytoplankton and a lower recycling efficiency in surface waters.

8.2.3 Terrestrial influence

The Rio Plata has a drainage basin of 3.2 x10$^6$ km$^2$ and is considered to be the fourth largest globally and second largest in South America following the Amazon. The Rio Plata outflow is characterised by high $\delta^{15}N_{\text{NO}_3}$ and $\delta^{15}N_{\text{PN}}$, which may suggest denitrification processes occurring in the estuary. A low $\delta^{13}C$ source associated with high particulate Al concentrations is identified on the western continental slope, indicating a supply of terrestrial derived C to the subsurface ocean. Although organic matter in sediments is principally marine derived, higher C:N ratios in Argentine sediments suggest that there is a source of terrestrial organic matter to this basin. These findings can be further investigated using $\Delta^{14}C$ and a suite of radionuclide measurements. The role of the Rio Plata estuary in supplying terrestrial organic matter to the open ocean remain unclear, highlighting the complexities of organic matter transformations at coastal boundaries.
8.3 Critical evaluation of research

Through this study isotope measurements have been used to critically analyse the N and C cycling processes occurring in the South Atlantic. The use of nitrate isotopes as integrative tracers of processes in distal areas can be utilised to investigate nitrogen cycling processes on a basin wide scale and gives the scope to analyse global N cycling processes. In this regard, the work carried out in this study provides new insight into the role of Atlantic N cycling processes and the importance of this on a global scale. The isotopic measurements of organic matter within the South Atlantic provide further information on localised C and N cycling processes which can further be investigated with the use of other trace element and isotopes (TEIs) used in the Geotraces programme.

As this work uses stable isotope measurements to determine the importance of different biogeochemical processes, the high precision of these measurements is critical. This work involved a substantial amount of method development to ensure the measurement error was low enough to draw the conclusions made in this work. Further work at the University of Edinburgh may continue to increase reproducibility to allow these isotopic measurements to be used in additional studies of the marine environment.

8.4 Impact and use of research results

This work provides new insight into the importance of nitrogen fixation in the Atlantic Ocean and can be used to further our understanding of the biogeochemical cycling of nitrogen in the ocean. With a growing number of modelling studies being used to determine the relative balance of the marine N cycle, the stable isotopes of nitrate can be used as additional constraints to stoichiometric parameters. This work has substantially increased the global data set of nitrate isotope measurements and contributes to the Geotraces consortium. In the future, these data may be used in modelling studies to understand more about global nitrogen cycling processes within the modern ocean.

Stable isotope measurements can be used to understand more about processes occurring in the palaeo-ocean. The critical evaluation of isotopic measurements of
nitrate and organic matter furthers the understanding of the processes which may fractionate N and C within the ocean and the applicability of certain palaeoproxies in understanding the palaeo-ocean.

8.5 Future research priorities in this field

The marine N and C cycles are inextricably linked, and are likely to respond to anthropogenic induced changes. A warming climate is likely to increase the extent of oxygen deficient zones within the ocean and thus may increase the extent of N loss. In addition Fe deposition to the ocean may be reduced with changes to the climate (Mahowald et al., 2006). Humans are currently fixing as much N as the marine biosphere, having significant impacts on coastal regions and atmospheric deposition rates (Duce et al., 2008; Gruber and Galloway, 2008). In this work it is found that marine N supply and loss are relatively balanced and negative feedbacks therefore may modulate future changes to the N cycle. Fe supply however is essential for supply of new N to the ocean and remains a dominant control on N$_2$ fixation rates. I postulate that higher rates of Fe input to the Atlantic basin provide a net source of new N to the global ocean. Fe supply to the oceans is predicted to decrease, which may impact the basin rates of global N addition.

Intermediate water masses play an important role in fuelling low latitude productivity and their formation is tightly coupled to the properties of the mixed layer in which they form (Sallee et al., 2013). Future climate forcing may affect these formation regions and the subsequent supply of nutrients to subtropical regions. The importance of these water masses for the growth of non-diazotrophs and diazotrophs highlight the need to investigate the extent of future changes and the biogeochemical responses that may occur.


9 References


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References


References


Appendices

1 IRMS adjustments and modifications

SUERC

The gas prep system was modified over a number of months to increase the precision of sample analysis. It was found that the GC performance was degrading over the run cycle, which caused N₂O and CO₂ peaks to converge as a result of water or CO₂ getting through the slush trap. Glass beads were added to the slush trap to increase its surface area which removed all the water present. Initially a nafion trap was added to the system to remove water but over subsequent runs, this was found to be restricting flow. It was subsequently removed from the system and a magnesium perchlorate trap was added to the top of the CO₂ (Carbosorb) trap. The chromatography immediately improved for the bacterial samples and prevented the multiple CO₂ peaks and peak merging compared to the previous set up used. The amount of CO₂ in gas tube samples was internally consistent, the result of a linearity/CO₂ interference effect, as smaller samples were heavier and larger samples lighter. It was found that when the sample loop valve was moved from the "freeze" position to the "sample" position, a burst of CO₂ was introduced probably the result of the sample loop being at neutral atmospheric pressure. The plumbing was modified to have a computer-controlled valve on the vent of the sample freeze circuit. This enabled the sample to remain pressurised during the warm-up stage, which decreased the size of the CO₂ peak. With these amendments to the system, the sample peaks were well separated from CO₂ peaks and consistent throughout the sample run.

University of Edinburgh

It was found that a memory effect was affecting the standard output values. This was observed in particular with the large isotopic range in standards, with the standards following USGS 32 (δ¹⁵N = +180), having heavier values than their typical values (Figure A1). From these initial tests it was clear that a small amount of the sample was left behind within the system and thus affected the next sample in the run. The first observed problem with the system set up was that the needle was pulling out of the sample vial before the inject mode which allowed air into the system. The tuning
was subsequently changed so that the inject mode was switched before the needle was pulled out. This improved the precision of values, but there was still an observed memory effect which was affecting the absolute isotopic ratios of the standards. It was hypothesised that there may have been a build-up of sample in the liquid nitrogen (LN$_2$) traps within each sample run. To test whether this may have had an effect, we heated the LN$_2$ traps after their exit from the Dewar. There was no significant change to the isotopic values measured. Back flushing of the system was the next proposed option for improving the set up. From additional study of the plumbing of the system, it was found that the needle and initial traps could be flushed by leaving the needle in the vial for as long as possible after switching to inject mode. This was carried out by changing the timing in which the needle was extracted from the vial from 690 seconds to 1440 seconds. This allowed the load mode to be flushed with He prior to the next sample within the run. This solved the memory effect problems and increased the precision and accuracy of standard measurements.

**Figure A1** An example of standard runs before and after back flush of purge and trap system. The memory effect of the initial set up is demonstrated by either lower or higher isotopic values for the first standard of each set – which represented contamination from the previous sample.
**2 Nitrate isotope data (JC068)**

Nitrate isotope data from JC068. Each CTD bottle used on the cruise had a unique GEOTRACES number; which can be used to compare data. All hydrographic data is available in the International Data Product for the GEOTRACES 40°S cruise.

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3 Nitrate isotope data (D357)

Nitrate isotope data from JC068. Each CTD bottle used on the cruise had a unique GEOTRACES number; which can be used to compare data. All hydrographic data is available in the International Data Product for the GEOTRACES 40°S cruise.

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4 Box Model Output

N$_2$ fixation vs. subsurface nitrate

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Atmospheric deposition calculations

Calculation of the maximum source from atmospheric deposition (defined in the table as AD). An isotopic value of -2‰ is used for atmospheric deposition and fluxes are estimated from Baker et al. (2010). The proportion from N$_2$ fixation (NF), subsurface nitrate (norm) and atmospheric deposition can be distinguished.

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5 $\delta^{18}O_{H_2O}$

Samples were analysed by James Wilkinson at the University of Oxford. Data provided by Gideon Henderson. AABW samples range between -0.33 and 0‰.

Figure A2 $\delta^{18}O_{H_2O}$ of deep water masses across the 40°S transect.
6 Model estimates

In the model we assume that 5‰ is the initial $\delta^{15}$N, although input to the low latitudes is $\sim$6.2‰ from partial consumption in the subantarctic, 5‰ accounts for the total remineralised product which should integrate $\delta^{15}$N over the course of its transport. As Rafter et al. (2013) outline the remineralised product in the Pacific changes from low values in the Southern Ocean, increases in the low latitudes and decreases further north. With this variability the isotopic composition of the remineralised product added should be an integrated value. We can therefore assume that the average $\delta^{15}$N from non diazotroph production is 5‰ and deviations in $\Delta(15$-$18)_{\text{remin}}$ should represent the overall influences of N$_2$ fixation and denitrification in each ocean basin.

Using a variety of input values, the rate of N$_2$ fixation required to balance the isotopic composition of remineralised nitrate was typically double the rate of pelagic denitrification. Model spreadsheet available on request.

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<td>66 Tg N yr$^{-1}$, 138.6 Tg N yr$^{-1}$</td>
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<td>2. Somes et al., 2012</td>
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<td>3. Atlantic estimate of 32Tg</td>
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## 7 Suspended particulates

### JC068

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