Subantarctic Mode and Antarctic Intermediate Water during the Present and Last Glacial Maximum

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SUBANTARCTIC MODE AND ANTARCTIC INTERMEDIATE WATER DURING THE PRESENT AND LAST GLACIAL MAXIMUM

By

Corinne A. Hartin

A DISSERTATION

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SUBANTARCTIC MODE AND ANTARCTIC INTERMEDIATE WATER DURING
THE PRESENT AND LAST GLACIAL MAXIMUM

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The formation of Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW) significantly contributes to the total uptake and storage of anthropogenic gases, such as CO$_2$ and chlorofluorocarbons (CFCs), within the world's oceans. SAMW and AAIW formation rates in the South Pacific are quantified based on CFC-12 inventories using data from WOCE, CLIVAR, and data collected in the austral winter of 2005. This thesis documents the first wintertime observations of CFC-11 and CFC-12 saturations with respect to the 2005 atmosphere in the formation region of the southeast Pacific for SAMW and AAIW. CFC-12 inventories are $16.0 \times 10^6$ moles for SAMW and $8.7 \times 10^6$ moles for AAIW, corresponding to formation rates of $7.3 \text{ Sv} \pm 2.1 \text{ Sv}$ for SAMW and $5.8 \text{ Sv} \pm 1.7 \text{ Sv}$ for AAIW circulating within the South Pacific. Inter-ocean transports of SAMW from the South Pacific to the South Atlantic are estimated to be $4.4 \text{ Sv} \pm 0.6 \text{ Sv}$. Thus, the total formation of SAMW in the South Pacific is approximately $11.7 \text{ Sv} \pm 2.2 \text{ Sv}$. These formation rates represent the average formation rates over the major period of CFC input, from 1970 to 2005. The CFC-12 inventory maps provide direct evidence for two areas of formation of SAMW, one in the southeast Pacific and one in the central Pacific. These CFC-derived rates provide a baseline with which to compare past and future formation rates of SAMW and AAIW.
Average formation rates for SAMW and AAIW in the South Pacific were calculated from the National Center for Atmospheric Research Community Climate System Model version 4 (NCAR-CCSM4), using CFC-12 inventories. These inventories and rates are compared to those calculated earlier from observations within the South Pacific. CCSM4 accurately simulates the southeast Pacific as the main region of formation for both SAMW and AAIW. Model formation rates in the South Pacific for SAMW are 3.4 Sv, about one-third of the observational rate. Shallow mixed layer depth and insufficient meridional transport of high CFC waters in CCM4 are probable reasons for lower formation rates for SAMW. However, for AAIW in CCSM4, a rate of 8.1 Sv is slightly higher than the observational rate including error. Increased inventories in CCSM4, particularly in the southwest and central Pacific, and higher surface inventories are the main reasons for greater formation rates of AAIW. This comparison of formation rates in observations and model is useful for understanding the uptake and transport of anthropogenic CO$_2$, by the model, as CFCs are used for calculating anthropogenic CO$_2$ inventories.

Lastly, it is important to understand how SAMW and AAIW have changed under differing climatic periods as compared to the present. Formation rates are calculated for SAMW and AAIW between the Last Glacial Maximum (LGM; 21,000 years ago) and preindustrial (PI) period in the South Pacific, using the NCAR Community Climate System Model version 3 (CCSM3). Water mass formation rates are computed from thermodynamic (surface fluxes) and dynamic methods. The thermodynamic method does not account for contributions from mixing, while the dynamic method measures the total rate at which water enters the permanent thermocline. Formation rates from surface fluxes tend to destroy the surface water formation of G-SAMW and G-AAIW. However, using the dynamic method, SAMW and AAIW over the South Pacific exhibit increased subduction rates from 4.3 Sv during the PI to 8.9 Sv during the LGM for SAMW, and 4.3 Sv during the PI to 8.3 Sv during the LGM for AAIW. Calculations of interior mixing between the surface and the permanent thermocline are responsible for the formation and transport of these water masses into the interior subtropical gyre. Despite a few
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properties and formation of SAMW and AAIW under differing climatic conditions. This
diagnosis is timely because of the inconclusiveness about modern and future changes in mode and
intermediate water formation, and its potential role in the sequestration of atmospheric CO$_2$. 
This dissertation is dedicated to Nanny, who gave me my wings to fly.

“The future belongs to those who believe in the beauty of their dreams.”
-Eleanor Roosevelt
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Chapter 1

Introduction: Subantarctic Mode Water and Antarctic Intermediate Water

1.1 Global importance of SAMW and AAIW

Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW) play an important role in the earth's heat, freshwater and carbon budgets, as well as the ventilation of the Southern Hemisphere subtropical gyres. SAMW and AAIW are large-volume, relatively cool water masses that sequester and store significant quantities of atmospheric gases, such as CO$_2$ and O$_2$ [e.g., Sabine et al., 2004; Mikaloff-Fletcher et al., 2006] (Figure 1.1).

Figure 1.1: Column inventory of anthropogenic CO$_2$ in the oceans (mol m$^{-2}$) from Sabine et al. (2004). Note the high inventory between 40 and 60°S due to the formation of SAMW and AAIW.

Across the global oceans, the second largest sequestration and storage of anthropogenic CO$_2$ occurs between 40 and 60°S, due to the formation of SAMW and AAIW. Half of the northward transport of anthropogenic CO$_2$ lies within SAMW...
and AAIW [Ito et al., 2010]. Along with the storage of CO₂, SAMW and AAIW also play a significant role in the transfer of nutrients needed to sustain the marine ecosystems fueling primary production [e.g., Gordon, 1986; Toggweiler et al., 1991; Fine et al., 2001; Sabine et al., 2002; Sarmiento et al., 2004]. SAMW and AAIW are also thought to be the single most important global source of O₂ to the thermocline and equatorial region [Toggweiler et al., 1991; Russell and Dickson, 2003]. Therefore, due to their large volumes, high gas concentrations, and a connection to each Southern Hemisphere Ocean, SAMW and AAIW may play an important role in regulating and modifying the uptake, transport and storage of CO₂ on various climate relevant time scales.

1.2 Global circulation of SAMW and AAIW

The formation and circulation of SAMW and AAIW are an important component of the upper branch of the meridional overturning circulation (MOC) [Schmitz, 1996; Sloyan and Rintoul, 2001a]. North Atlantic Deep Water exported to the Southern Ocean is in part balanced by the formation and transport northward of SAMW and AAIW [Gordon, 1986; Sloyan and Rintoul, 2001a]. SAMW and AAIW are transported eastward within the Antarctic Circumpolar Current (ACC) and are transported northward into the Indian, Pacific, and Atlantic subtropical gyres [e.g. Talley, 2003; Speich et al., 2007].

The coldest, freshest, and densest variety of SAMW is formed in the southeast Pacific, just west of the Drake Passage [McCartney, 1977; 1982]; the main region supplying both SAMW and AAIW to the Pacific. A portion of these intermediate waters
(SAMW and AAIW) are transported equatorward within the Pacific where they upwell and warm, some flowing in the Indonesian Throughflow and returning as the "warm water path" to the Atlantic through the Agulhas Current [Gordon, 1986]. Still other portions of the mode and intermediate waters (SAMW and AAIW) are transported with the Antarctic Circumpolar Current and returned to the Atlantic through the Drake Passage as the "cold water path" [Rintoul, 1991; Macdonald, 1993; Schmitz, 1995].

SAMW and AAIW enter the Indian subtropical gyre at several longitudes. The northward transport of SAMW and AAIW into the subtropical gyre is associated with weakening of the South Indian Ocean Current at 50°E, 65°E, 90°E, and 100°E into the Perth Basin [Stramma, 1992; Fine, 1993; Toole and Warren, 1993]. The Kerguelen Plateau (70–80° E) represents the boundary between two varieties of SAMW, with significantly higher CFC and oxygen levels in the mixed layer on the eastern side of the Plateau [Fine, 1993; Talley, 1999]. This is the dominate source of SAMW in the Indian Ocean [Sallee et al., 2006].

In the Atlantic Ocean, SAMW and AAIW are transported northward with the Malvinas Current, west of 60° W, where they encounter less dense waters and progressively sink to occupy depth at 800–1000 m [McCartney, 1977]. However, these waters do not enter the subtropical gyre due to the southward flowing Brazil Current. SAMW and AAIW are transported into the subtropical gyre along the eastern boundary where part of the South Atlantic Current turns northward, feeding the Benguela Current [Stramma and Peterson, 1990; Peterson and Stramma, 1991].

Recent studies have suggested the importance of SAMW and AAIW within a supergyre, circulating and connecting the South Pacific and South Indian Oceans
[Ridgway and Dunn, 2007; Speich et al., 2007]. This supergyre concept allows for ocean to ocean exchange of water masses and properties [Roemmich, 2007]. The northward transport of SAMW and AAIW from the South Atlantic, South Indian Ocean, and South Pacific currents injects cold, fresh mode and intermediate water into each subtropical gyre. In the western Brazil, Agulhas, and East Australian Currents, modified warm, salty mode and intermediate water are returned to the Southern Ocean. The exchange of “new” mode and intermediate water with “older” mode and intermediate water represents a mechanism by which Antarctic upper waters ventilate the subtropical gyres.

1.3 AAIW properties, circulation and formation

Circumpolar Deep Water upwells around Antarctica and is carried northward via Ekman transport as Antarctic Surface Water (AASW). AASW is subsequently converted to AAIW through air-sea fluxes equatorward of the Polar Front (PF), and subducts at the Subantarctic Front [ SAF; e.g., Sloyan and Rintoul, 2001b], circulating to the north and west via the Pacific subtropical gyre and eastward along the ACC [Santoso and England, 2004]. AAIW is characterized by low temperatures, a vertical salinity minimum (Figure

**Figure 1.2:** Salinity depth profile along 88°W, from 1993. Black contours represent the isopycnals of SAMW and AAIW in the South Pacific. Note the strong salinity minimum that extends to the equator between 27.06 and 27.4 kg m$^{-3}$ sigma-theta.
1.2) and high oxygen concentrations between 600 and 1100m within all three Southern Hemisphere oceans [e.g., Reid, 1986; Hanawa and Talley, 2001]. The low salinity core of AAIW can be recognized as far north as 20°N in both the Atlantic and Pacific Oceans [Talley, 1999] (Figure 1.3).

There have been several theories proposed on the formation of AAIW. Deacon [1937] suggested that the circumpolar formation of AAIW was the result of subduction of AASW below the SAF. This idea of circumpolar formation has been replaced by theories that suggest that the renewal of AAIW occurs in specific regions of the Southern Ocean, in particular, the southeast Pacific and the southwest Atlantic [McCartney, 1977; Georgi, 1979; Molinelli, 1981; Piola and Georgi, 1982; Piola and Gordon, 1989].

Figure 1.3: Global distribution of salinity minimum. AAIW highlighted in the bright green extends out to 20°N in both the Pacific and Atlantic Oceans, with Labrador Sea Water and North Pacific Intermediate Waters being the other large intermediate water masses. The ‘X’in the South Pacific represents the main location of the formation of AAIW.
appears to be a consensus that AAIW is renewed in the southeast Pacific and southwest Atlantic, but there is some debate on the formation mechanisms involved.

McCartney [1977] suggests that the formation of AAIW is linked to SAMW. He shows that SAMW and AAIW in the southeast Pacific and southwest Atlantic regions have identical T–S properties. However, Molinelli [1981] suggests that AAIW is formed by isopycnal exchange across the PF with significant inputs near Kerguelen Island (80°E) and in the southeast Pacific. Georgi [1979] and Piola and Georgi [1982] identify two separate pools of AAIW, one in the southeast Pacific and southwest Atlantic. These studies support McCartney’s [1977] idea of AAIW renewal in the southeast Pacific, but in the southwest Atlantic suggest that AAIW is produced near the Polar Front as proposed by Molinelli [1981]. Piola and Gordon [1989] show a connection between AAIW in Drake Passage and in the southwest Atlantic. They find that the modification of Drake Passage AAIW to colder, fresher AAIW in the southwest Atlantic can be explained by a combination of further deep winter mixing and exchange of AASW across the PF. This combines both theories of McCartney [1977] and Molinelli [1981]. More recently, Sloyan and Rintoul [2001b], support the theory proposed in Piola and Gordon [1989] of formation in the southeast Pacific and transport into the Atlantic.

**1.4 SAMW properties, circulation and formation**

Equatorward of AAIW formation, SAMW is formed from the deepening of mixed layers during wintertime convection [Aoki et al., 2007; Holte et al., 2012] and subsequent mixing [Sloyan et al., 2010]. SAMW occupies the lower pycnocline of the Southern Hemisphere subtropical gyres and is characterized by a vertically homogenous layer of low potential vorticity (Figure 1.4). SAMW is formed north of the SAF throughout the
southern hemisphere, with the main site of formation in the southeast Pacific
[McCartney, 1977; Hartin et al., 2011]. SAMW is progressively cooled and freshened
along its circumpolar path by deep winter mixing events, resulting in the coldest freshest
SAMW in the southeast Pacific [McCartney, 1977]. The warmest and most saline
SAMW is formed in the South Atlantic. The density of SAMW changes gradually across
the oceans with large changes occurring in the transition regions south of South America,
Africa, and New Zealand [Piola and Georgi, 1982]. There is a wide variation in the
thickness of SAMW, with the thickest layers being found in the eastern South Indian
Ocean and across the South Pacific Ocean [Hanawa and Talley, 2001].

![Figure 1.4: Potential vorticity (m$^{-1}$s$^{-1}$) depth profile along 88°W, from 2005. Black contours represent the isopycnals bounding SAMW in the South Pacific. Note the strong potential vorticity minimum between 26.8 and 27.06 kg m$^{-3}$ sigma-theta. This potential vorticity minimum is associated with deep mixed layers, >500 meters, in the SAMW formation region of the southeast Pacific.](image)

Different forcing mechanisms drive the formation of SAMW in the Subantarctic
Zone (SAZ), the region between the Subtropical Front and the Subantarctic Front (SAF).
Ekman pumping in the SAZ favors the formation of deep-mixed layers associated with
SAMW. The combined effect of air–sea fluxes and Ekman transport are mainly
responsible for SAMW formation [e.g. McCartney, 1977; Sloyan and Rintoul, 2001b;
Rintoul and England, 2002]. Eddy heat diffusion causes local cooling or warming of SAMW and mixing preconditions the water column for formation [Sallee et al., 2008; Sloyan et al., 2010].

1.5 Variability in SAMW and AAIW

1.5.1 20th Century variability in SAMW and AAIW in the South Pacific Ocean

Variations in surface properties of the Southern Ocean are communicated through the subtropical gyres of the Southern Hemisphere by SAMW and AAIW. Changes in mode and intermediate water masses are a recurrent outstanding feature in model projections of present and future climate change [e.g., Fyfe et al., 2007; Liu and Wu, 2012]. However, the general lack of observations in the South Pacific poses a serious challenge to the detection of variability in these waters. Chapters 2 and 4 use the available hydrographic data and model output to estimate average formation rates, over the period of 1970-2005, for SAMW and AAIW in the South Pacific. These decadal average rates will allow for future variability of SAMW and AAIW to be diagnosed. This section will focus on current observations in variability in SAMW and AAIW.

Using temperature measurements obtained over eight decades (1930s–2000s), Gille [2002; 2008] reported an extensive warming of the upper kilometer of the water column around the northern edge of the ACC (both SAMW and AAIW) between the 1950s and the 1980s. The warming doubled the global-mean trend for that depth range, and it continued at a lesser rate into the 2000s.

Possibly related to this widespread warming, instances of regional variability in mode and intermediate water masses have been documented by several studies. In the
Pacific Ocean, AAIW showed significant freshening of 0.021 on the density surface along the 17°S Pacific sections, when data are compared from 1930-1980 with data from 1985-1994 [Wong et al., 1999]. One explanation is an increase in precipitation minus evaporation for the high latitudes of the Southern Ocean. Wong et al. [1999] extrapolated the freshening signal of AAIW (0.021 over 500 m) across the entire South Pacific to determine that the freshwater flux at the source region of AAIW has to increase by approximately 31 mm/yr between the latitudes of 55°S and 65°S. This translates to 8.5% of the yearly precipitation at 55°S. Morgan et al. [1991] using Antarctic ice cores showed that snow accumulation had increased since the 1960s by approximately 23%, potentially the reason for the observed freshening signal of AAIW. Surface salinities have freshened at all latitudes, along with precipitation increasing poleward of 45°S and equatorward of 10°S [Banks and Bindoff, 2003]. These observations potentially provide evidence for an intensification of the global hydrological cycle due to increased anthropogenic forcing.

Banks and Bindoff [2003], when comparing data from the early 1960s to the early 1990s, observed a pattern of cooling and freshening along AAIW isopycnals (27.0-27.4 kg m⁻³) in the Pacific Ocean, suggesting a fingerprint of anthropogenic forcing. Surface temperatures have increased at all latitudes except north of 65°S in the Pacific, suggesting significant heat uptake by the oceans [Banks and Bindoff, 2003]. They compared the data with a model simulation and investigated the mechanisms responsible for the variability observed in the AAIW. They interpreted the signal as due to anthropogenic forcing of increasing the temperature or freshwater flux to the surface at the primary regions of AAIW formation. Johnson and Orsi [1997] also observed
freshening and cooling on isopycnals of -0.25°C and -1°C along the base of the subtropical gyre thermocline between 1968 and 1991 in the western South Pacific. Bindoff and Church [1992] observed significant freshening and cooling on neutral density surfaces and warming on isobars along 43°S and 28°S. The observed temperature changes along neutral density surfaces are the largest along 43°S, which is consistent with the idea that these waters having been recently ventilated. This is different from changes observed along 28°S, where waters reside within the Pacific subtropical gyre circulation much longer [Bindoff and Church, 1992].

However, along 32°S in the Pacific Ocean within the salinity minimum of AAIW between 1992 and 2003, Schneider et al. [2005] observed an increase in temperature and salinity by 0.095°C and 0.0041, respectively. This reverses a decrease in salinity along AAIW isopycnals shown by Wong et al. [1999], suggesting that these changes may be due to natural oscillations in the climate system.

1.5.2 SAMW and AAIW during the Last Glacial Maximum

Variability of SAMW and AAIW has also been documented on glacial-interglacial time scales. Chapter 4 focuses on understanding the physical mechanisms responsible for the apparent changes in SAMW and AAIW during the Last Glacial Maximum (LGM) in a climate model. The LGM represents an extreme example for analyzing changes to the climate system. This diagnosis is timely because of the inconclusiveness about modern and future changes in intermediate water formation, and its potential role in CO₂ sequestration and transport of O₂ and nutrients to the equatorial regions. This chapter investigates the competing processes of upper ocean stratification
and wind stress on the formation of SAMW and AAIW, both projected to increase under future climate change [i.e., Russell et al., 2006; Fyfe et al., 2007].

The climate of the LGM (~21,000 years ago) was characterized by globally cooler temperatures and increased ice sheet cover [Adkins et al., 2002; Peltier, 2004]. Atmospheric $pCO_2$ was at 180-200 ppm, or 80-100 ppm lower than preindustrial values [Petit et al., 1999; Monnin et al., 2001]. During the LGM there was a fundamental reorganization of the global ocean circulation, with major shifts in the transfer of $CO_2$ between the oceans and atmosphere. Past changes in global atmospheric $CO_2$ concentrations over glacial and interglacial cycles are believed to be driven by two processes; physical, e.g. ventilation and stratification changes of intermediate to deep waters, and biological, e.g. changes in nutrient distributions and biological productivity [Siegenthaler and Wenk, 1984; Francois and Altabet, 1997; Sigman and Boyle, 2000; Toggweiler et al., 2006].

Detailed paleo-proxy studies of SAMW and AAIW in the LGM are limited, especially within the South Pacific. Sediment core studies within the eastern South Pacific and equatorial Pacific of the LGM suggest increased ventilation and increased production of AAIW. Muratli et al. [2010], using rhenium and manganese concentrations in sediments along the Chilean margin, concluded that AAIW production and oxygen concentrations increased in the LGM. Nameroff et al. [2004] attributed changes in redox sensitive trace metals along the Mexican continental margin oxygen minimum zone to changes in regional export production and or changes in ocean circulation, with these changes traced back to SAMW. Using a combination of nutrient proxies and $\delta^{13}C$ and $\delta^{18}O$, Matsumoto et al. [2002] interpreted the data as showing increased formation rates.
of SAMW and AAIW in the Pacific during the LGM. In the western Pacific, Bostock et al. [2004; 2010] used benthic foraminiferal $\delta^{13}$C, to show that AAIW was a thicker, more dominant water mass in the LGM with increased influence on the equatorial regions. This also agrees with a study by Lynch-Steiglitz et al. [1994] who concluded that transport of salty Indian waters along the ACC was reduced to the western Pacific in the LGM, and replaced by more poleward sourced surface waters and AAIW production there.

Proxy studies using $\delta^{15}$N have identified areas of reduced denitrification in both the North and South Pacific during the LGM. The reduction was due to a combination of lower glacial temperatures, increasing O$_2$ solubility, and enhanced ventilation of thermocline waters [Kienast et al., 2002; Galbraith et al., 2004; Nameroff et al., 2004]. Support for this comes from a modeling study by Meissner et al. [2005] who found enhanced production and transport of O$_2$ rich thermocline to intermediate waters into the eastern tropical Pacific, thereby reducing the denitrification zones during the LGM. However, there is some debate that the lower denitrification rates in the equatorial Pacific in the LGM were due to decreased input of nitrate from the Southern Ocean, rather than changes in water mass ventilation [Robinson et al., 2007; Robinson et al., 2009]. Though limited in number and distribution, available paleo-proxy studies point to significant increases in the circulation and ventilation of SAMW and AAIW in the LGM.
1.6 An introduction to chlorofluorocarbons as oceanic tracers

Three out of four of the main science chapters contained within this dissertation use chlorofluorocarbons (CFCs) to estimate water mass formation rates from observations and global coupled climate models. CFCs were used in the mid-20th Century as coolants in refrigerants and air conditioners, propellants in aerosol cans and foaming agents. Walker et al. [2000] reconstructed the atmospheric mole fractions for CFC-11 and CFC-12 in both the Northern and Southern Hemispheres from observations made by the Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment/Advanced Global Atmospheric Gases Experiment Program (Figure 1.5). CFC-11 and CFC-12 have atmospheric lifetimes of 45 and 100 years, respectively [Walker et al., 2000]. The mixing ratio of these gases increased exponentially at the beginning of their

![Graph showing annual atmospheric dry air mole fraction of CFC-11 and CFC-12 in the Southern Hemisphere from 1931 to 2006.](image)
production, and then increased more linearly in the 1970s and 1980s. In the 1990’s the concentrations of CFC-11 began to decrease in the Northern Hemisphere due to the phase out of these compounds in industrial use under the signing of the Montreal Protocol in 1987. Industrial production of CFCs was larger in the Northern Hemisphere than in the Southern Hemisphere resulting in a gradient between the hemispheres of about 8% [Fine et al., 2001]. The errors associated with CFC-11, and CFC-12 are small, because they have a relatively well know industrial emission record. Since CFCs are used as a time tracer of ocean circulation, it is important to evaluate the errors in the atmospheric concentrations because these uncertainties are translated into errors within oceanic measurements [Fine et al., 2001].

Willey et al. [2004] constructed an oceanic inventory of CFC-11 dissolved in the oceans (Figure 1.6). Approximately 1% of the total CFC-11 emissions through 1994 are dissolved in the oceans and 82% of the CFC-11 inventory is within the upper 1000 meters [Willey et al., 2004]. More than 60% of the total CFC-11 inventory is in the Southern Hemisphere, due to the ventilation of SAMW and AAIW.

An important factor in using CFCs as tracers of circulation is that they are conservative; giving rates of diapycnal/isopycnal mixing and advection [Lee et al., 1999] with negligible chemical and biological decomposition on decadal time scales. Studies have shown a pronounced depletion in CFC-11 in subsurface anoxic zones and in deep anoxic hydrogen sulfide water [Bullister and Lee, 1995; Lee et al., 1999]. CFC-12 behaves conservatively throughout the water column in highly anoxic basins [Lee et al., 1999]. In a 2.8 year incubation period in oxygenated waters, both CFC-11 and CFC-12
were persistent [Lee et al., 1999], thereby confirming that CFCs are conservative tracers in oxygenated waters.

1.6.1 Partial pressure age

Since CFCs are conservative tracers, a partial pressure age of the water mass can be calculated. CFC concentrations in the oceans are expressed in terms of their partial pressure (pCFC). This is the concentration of CFC divided by the saturation of the gas with respect to the present atmosphere. Saturation is influenced by temperature, salinity and wind speed. These pCFC values are adjusted for the surface saturations, assuming that the surface waters when in contact with the atmosphere were in equilibrium with the

**Figure 1.6**: Map of vertically integrated CFC-11 in moles km$^{-2}$ from Willey et al. [2004]. The highest values are in red and the lowest are in blue. The + symbol shows station locations. Note the similarity between the anthropogenic inventory in Figure 1.1.
atmosphere. The pCFCs values are then matched to the atmospheric time history and a year of formation is assigned to the water mass [Fine et al., 2001]. A limitation of this technique is assuming that when the parcel of water was in contact with the atmosphere it was at equilibrium. Therefore, to accurately calculate the partial pressure age of the water mass, the percent saturation should be measured during the time of water mass formation in late winter.

1.6.2 Solubility

The percent saturations are dependent upon the solubility of CFCs in surface waters. The concentration of CFCs in solution is related to the partial pressure through Henry’s law $p_i = k_i[i]$, where $[i]$ is the concentration of the dissolved CFCs and $k_i$ is the solubility constant, dependent on temperature, pressure, salinity and the gas. When $p_i$ of the water equals $p_i$ of the atmosphere, the gas is in equilibrium. The solubility of CFCs increases with decreasing temperature at a rate of approximately 4% for 1°C [Warner and Weiss, 1985]. When comparing CFCs to oxygen, at a constant salinity the temperature effect on solubility is twice as great for CFCs.

Warner and Weiss [1985] and Bu and Warner [1995] measured experimental values of $k_i$ for CFC-11 and CFC-12 at varying temperatures and salinities and fit to this equation; $C^* = k_i x_i (P - p_{H_2O})$, where $C^*$ is the equilibrium concentration of the dissolved CFCs, $k_i$ is the solubility constant, $x_i$ the dry air mole fraction, $P$, pressure and $p_{H_2O}$ the water vapor pressure. The solubility function, $F$, can be calculated from the equation $F = C^*/x_i$ or $F = k_i (P - p_{H_2O})$. 
1.6.3 Air-sea exchange

The surface mixed layer gas saturations are also influenced by the interactions at the air-sea interface. In a simplified model of air-sea gas exchange there is a turbulent atmosphere layer (Cg) with uniform partial pressure, a turbulent liquid layer (Cl) again with uniform partial pressure and then a laminar layer in between [Liss and Slater, 1974]. This laminar layer is the major resistance to exchanges of gas across the air-sea interface.

\[ F = -D \frac{\partial c}{\partial z} \]

represents the flux of gases across the interface, Fick’s First Law, D is the molecular diffusion coefficient and c is the concentration of the gas. The equation can be written as, \( F = k\Delta c \), where \( \Delta c \) is the concentration gradient across the interface and \( k = D/z \), where k is the measure of the flux of gas per unit concentration gradient. The values of k in Fick’s Law depend on the turbulence in the gas and liquid layers. Wind speed, boundary layer stability, surfactants and bubbles play a major role in influencing the gas transfer rate [i.e., Wanninkhof; Ho et al., 2011]. In regions of high westerly winds in the high latitudes during the winter, there is a great potential for increased air-sea exchange. However, due to the formation of deep mixed layers, these waters may not come into equilibrium with the present atmosphere.

1.6.4 Mixed layer depth

Mixed layer depth plays an important role in the equilibration of CFCs with the atmosphere. The mixed layer is defined as the layer in contact with the atmosphere where the salinity, temperature and density are vertically homogenous. The base of the mixed layer represents a sharp change in these properties. The mixed layer is formed from vigorous turbulent mixing [Montegut et al., 2004] in the upper surface waters. There is significant transfer of mass, momentum and energy across this layer and the
depth of the mixed layer determines the amount of heat directly interacting with the atmosphere. This transfer of energy and momentum to the surface ocean is a driving factor in oceanic surface currents.

**Figure 1.7:** CFC-11 saturations with depth along 88°W in 2005. Mixed layer depths plotted in in the dash dot line, > 400 m. The lower boundary of SAMW, sigma-theta surface 27.06, is plotted in the dashed line.

Mixed layers are the boundary between the interior ocean and the atmosphere. This yearly process ventilates the thermocline and carries properties of the water masses into the interior [Montegut et al., 2004]. For example, SAMW is formed within >500 m mixed layers in the southeast Pacific [Holte et al., 2012] (Figure 1.7). Haine and Richards [1995], showed that the controlling factors in the CFC saturations are the seasonality of the mixed layer and the maximum depth of the mixed layer overturning.

In recent observations of intermediate waters in their formation regions, CFC-12 and CFC-11 have not been fully equilibrated with the atmosphere. Wallace and Lazier
[1988] reported 60% saturation of Labrador Sea Water with respect to atmospheric conditions in their recently ventilated, 1500 m mixed layer. Therefore, assuming 100 percent saturation with the atmosphere at the time of formation can be inaccurate when using CFC-11 and CFC-12. It is important to measure the saturations during the time of formation in order to accurately obtain a ventilation age for the water mass being studied. If the water mass does not come into equilibrium with the present atmosphere, then the age of water subducted will not have been re-set to zero.

1.7 Outline of thesis chapters

This dissertation is divided into four science chapters:

- Chapter 2: Estimate rates of formation for SAMW and AAIW in the southeast Pacific, and their inter-oceanic transports using a combination of World Ocean Circulation Experiment (WOCE), Climate Variability and Predictability (CLIVAR), and recently collected hydrographic and chlorofluorocarbon (CFC) data in the southeast Pacific (SAMFLOC). This work is published in Deep Sea Research [Hartin et al., 2011].

- Chapter 3: Assess Southern Hemisphere CFC uptake within National Center for Atmospheric Research (NCAR) Community Climate System Model version 4 (CCSM4). This work is published in part in [Weijer et al., 2012].

- Chapter 4: Estimate rates of formation of SAMW and AAIW in the southeast Pacific within NCAR-CCSM4 to compare to the observations in Hartin et al. [2011]. This work is submitted to the Geophysical Research Letters [Hartin et al., submitted].
Chapter 5: Assess the physical mechanisms (i.e. buoyancy fluxes and subduction) responsible for the changes in SAMW and AAIW during the Last Glacial Maximum (LGM), using the National Center for Atmospheric Research (NCAR) Community Climate System Model version 3 (CCSM3). The focus is on changes between the preindustrial (PI; ~1870 A.D.) and LGM on SAMW and AAIW in the South Pacific. This work is currently in draft form to be submitted to the Journal of Climate.
Chapter 2

Formation Rates of Subantarctic Mode Water and Antarctic Intermediate Water in the South Pacific

2.1 Background

The formation of Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW) significantly contributes to the total uptake and storage of anthropogenic gases, such as CO$_2$ and chlorofluorocarbons (CFCs), within the world's oceans. SAMW and AAIW formation rates in the South Pacific are quantified based on CFC-12 inventories using hydrographic data from WOCE, CLIVAR, and data collected in the austral winter of 2005. This study documents the first wintertime observations of CFC-11 and CFC-12 saturations with respect to the 2005 atmosphere in the formation region of the southeast Pacific for SAMW and AAIW. SAMW is 94% and 95% saturated for CFC-11 and CFC-12 and AAIW is 60% saturated for both CFC-11 and CFC-12. SAMW is defined from the Subantarctic Front to the equator between potential density 26.80 - 27.06 kg m$^{-3}$, and AAIW is defined from the Polar Front to 20°N between potential densities 27.06 - 27.40 kg m$^{-3}$. CFC-12 inventories are 16.0x10$^6$ moles for SAMW and 8.7x10$^6$ moles for AAIW, corresponding to formation rates of 7.3 Sv ± 2.1 Sv for SAMW and 5.8 Sv ± 1.7 Sv for AAIW circulating within the South Pacific. Inter-ocean transports of SAMW from the South Pacific to the South Atlantic are estimated to be 4.4 Sv ± 0.6 Sv. Thus, the total formation of SAMW in the South Pacific is approximately 11.7 Sv ± 2.2 Sv. These formation rates represent the average formation rates over the major period of CFC input, from 1970 to 2005. The CFC-12 inventory maps provide direct evidence for two areas of formation of SAMW, one in the southeast Pacific and one in the central Pacific.
Furthermore, eddies in the central Pacific containing high CFC concentrations may contribute to SAMW and to a lesser extent AAIW formation. These CFC-derived rates provide a baseline with which to compare past and future formation rates of SAMW and AAIW.

### 2.2 Introductory remarks

Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW) are large-volume relatively cool water masses, which in their formation regions sequester significant quantities of atmospheric gases, e.g. CO$_2$ and chlorofluorocarbons (CFCs) [Fine et al., 2001; Sabine et al., 2004; Willey et al., 2004]. Past changes in global atmospheric CO$_2$ concentrations over interglacial and glacial cycles may have been driven by changes in ventilation and circulation of intermediate and deep waters [e.g., Siegenthaler and Wenk, 1984; Francois and Altabet, 1997; Toggweiler, 1999]. In the present ocean, the formation and circulation of SAMW and AAIW are an important component of the upper branch of the meridional overturning circulation (MOC), involved in the transport of heat and salt within the southern hemisphere subtropical gyre [Schmitz, 1996; Sloyan and Rintoul, 2001a; Talley, 2003; 2008].

There are numerous processes that influence the formation and properties of SAMW and AAIW such as convection within mixed layers due to air-sea fluxes, Ekman transport, eddy fluxes, and mixing within the Subantarctic Front (SAF) [McCartney, 1982; Sloyan and Rintoul, 2001b; Sloyan et al., 2010; Sallee et al., 2010]. Circumpolar Deep Water upwells around Antarctica and is carried northward via Ekman transport as Antarctic Surface Water (AASW). AASW is converted to AAIW through air-sea fluxes
equatorward of the Polar Front (PF) and subducts at the Subantarctic Front (SAF) [e.g., Sloyan and Rintoul, 2001b]. AAIW is characterized by a vertical salinity minimum and observed in the southern hemisphere oceans between 600 and 1100 m [e.g. Hanawa and Talley, 2001]. Equatorward of AAIW formation, SAMW is formed from the deepening of mixed layers during wintertime convection [Holte et al., 2012] and subsequent mixing (Sloyan et al., 2010), and is found north of the SAF throughout the southern hemisphere. SAMW is characterized by a minimum in potential vorticity. It occupies the lower pycnocline of the southern hemisphere subtropical gyres. As a consequence of the formation process, both SAMW and AAIW have relatively high gas concentrations – oxygen, CO$_2$ and CFCs. SAMW and AAIW are transported eastward with the Antarctic Circumpolar Current (ACC) and northward into the Indian, Pacific, and Atlantic subtropical gyres. The coldest and freshest varieties of SAMW and AAIW are formed in the southeast Pacific [McCartney, 1977; 1982], the main region supplying SAMW and AAIW to the Pacific.

Chlorofluorocarbons (CFC-11 and CFC-12) are oceanic tracers used to evaluate circulation patterns, ages, and formation rates of water masses [e.g., Fine, 2011]. CFCs are anthropogenic compounds that have been continuously added to the atmosphere since the 1930s. The concentrations have been continually increasing in the atmosphere up to the late 1990s for CFC-11 and to the early 2000s for CFC-12. The largest increase in concentration has occurred since the 1970s. CFCs enter the surface ocean from the atmosphere by gas exchange, with an average equilibration time of about 1 month [Broecker et al., 1980]. Once they become isolated from the atmosphere, CFC concentrations are stable in the ocean interior, except for the effects of mixing with
waters of different concentrations. Most surface waters are found to be close to saturation with respect to the atmosphere. However, this varies in regions of deep convection and vertical mixing, where mixed layers maybe too deep to maintain equilibrium with the atmosphere [Smethie and Fine, 2001]. It is the surface saturations together with total inventories of CFCs that are critical in calculating the ages and formation rates of water masses.

In this study, we use the first austral wintertime observations of CFC-12 concentrations in the southeast Pacific for SAMW and AAIW to determine the percent saturation of CFC-11 and CFC-12 relative to the present atmosphere. Formation rates are calculated for SAMW and AAIW from 1970 to 2005. Formation rates are directly related to the percent saturation during winter water mass formation and to the total inventory of CFCs within each water mass. Inter-oceanic transports of SAMW and AAIW are calculated to estimate the potential loss of SAMW and AAIW out of the South Pacific through the Drake Passage. This paper will also address the location of formation areas of SAMW and AAIW, and the possible impact of eddies on formation of SAMW and AAIW within the South Pacific. Finally, SAMW and AAIW in the South Pacific will be compared with mode and intermediate waters globally.

2.3 SAMW and AAIW in the South Pacific

2.3.1 Hydrographic and chlorofluorocarbon data

World Ocean Circulation Experiment (WOCE) and Climate Variability and Prediction (CLIVAR) tracer and hydrographic data, and data collected on board the R/V Knorr between August and October of 2005 in the southeast Pacific [SAMFLOC;
Chereskin, 2005] are used in this analysis (Figure 2.1). [Data are available at http://cchdo.ucsd.edu/]. The WOCE and CLIVAR observations date from 1989 to 2006, and are located between 70°S to 20°N and 70°W to 150°E. A total of 4732 individual CFC-12 measurements at 327 stations are used in the inventory calculation for SAMW, and 5558 individual CFC-12 measurements at 355 stations for AAIW. Challenges associated with combining data from multiple years are discussed in section 2.4.1.

Figure 2.1: Map of the South Pacific with grayscale shading representing bottom bathymetry (m) from ETOPO2. Diamonds represent the location of the hydrographic profiles from WOCE and CLIVAR with 150°W occupied during 1991 and 2005, and the crosses represent the station locations from the 2005 SAMFLOC cruise. The number 1 identifies the location of the Campbell Plateau and number 2 identifies the Eltanin Fracture Zone.

2.3.2 Water mass boundaries

To calculate the CFC-12 inventories within SAMW and AAIW, water mass boundaries were determined from examining the WOCE, CLIVAR, and the 2005 SAMFLOC data. Boundaries were chosen based on a combination of numerous parameters including: temperature, salinity, potential vorticity (a measure of the stratification of a water mass), nutrients, oxygen, CFC-11 and CFC-12 concentrations and
saturations (Table 2.1). SAMW lies between potential densities ($\sigma_0$) $26.80 < \sigma_0 \leq 27.06$ kg m$^{-3}$ and is characterized by a minimum in potential vorticity, outcropping north of the SAF and forming within mixed layers exceeding 400 m during the austral winter (Figure 2.2a). SAMW subducts to a depth of ~ 600 m, and is integrated into the subtropical gyre of the South Pacific. The isopycnal 26.80 kg m$^{-3}$ separates SAMW from the less dense thermocline waters of the South Pacific. The isopycnal 27.06 kg m$^{-3}$ is the base of the potential vorticity minimum and also separates SAMW from the denser AAIW found between $27.06 < \sigma_0 \leq 27.20$ kg m$^{-3}$. Other observational studies have defined SAMW and AAIW on similar density surfaces. For example, Tsuchiya and Talley [1998] define SAMW between 26.9 and 27.1 $\sigma_0$ and AAIW between 27.0 and 27.35 $\sigma_0$ along 88°W in the South Pacific. AAIW is characterized by a salinity minimum, outcropping at the Polar Front (PF) during austral winter and subducting to depths of 1100-1200 m. Figure 2.2b shows the low salinity signal of AAIW within the upper few hundred meters after subducting at the SAF. As AAIW is transported equatorward within the subtropical gyre, the density increases and the salinity minimum broadens in density from 27.06 - 27.40 kg m$^{-3}$ [e.g. Reid, 1965].

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<th>Potential Temperature °C</th>
<th>Salinity psu</th>
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<th>CFC-11 pmol kg$^{-1}$</th>
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</table>

Table 2.1: Average properties of SAMW and AAIW from the SAMFLOC 2005 austral winter data in the southeast Pacific from approximately 76°W to 100°W and from 60°S to 45°S. Average properties are taken when the density range for SAMW is within the mixed layer, and average properties for AAIW are taken within the density range for AAIW, north of the SAF.
Figure 2.2: Depth sections along 88° W from August 2005 of a) potential vorticity and b) salinity. SAMW lies between 26.8 - 27.06 kg m$^{-3}$, AAIW lies between 27.06 - 27.2 kg m$^{-3}$ and extends down to 27.4 kg m$^{-3}$ within the subtropical gyre. The location of the SAF is found at the outcrop of 27.06 kg m$^{-3}$, approximately 59°S.

2.3.3 CFC and oxygen saturations in the southeast Pacific in austral winter 2005

This is the first study to document CFC-11 and CFC-12 saturations in SAMW and AAIW in austral winter in the southeast Pacific. Saturations are calculated (Warner and Weiss, 1985) from the 2005 winter data by comparing the measured oceanic concentrations to the atmospheric concentrations from the ALE/GAGE/AGAGE network (http://cdiac.ornl.gov/ndps/alegage.html), a global network of trace atmospheric gas measurements. In this paper, surface waters represent the upper 10 m of the water column.
From the austral winter 2005 SAMFLOC data, we observe average CFC-11, CFC-12 and \( \text{O}_2 \) surface saturations (not shown) poleward of the SAF to be slightly undersaturated. Within the mixed layers of SAMW (26.80 and 27.06 kg m\(^{-3}\)), CFC-11 and CFC-12 are 94% and 95% saturated with respect to the 2005 atmosphere (Figure 2.3a), respectively. Within the core of AAIW (27.20 kg m\(^{-3}\)) poleward of the SAF, AAIW is 85% saturated in CFC-12 relative to the present atmosphere (Figure 2.3b), and average oxygen saturations are 79%. Once AAIW subducts at the SAF, average CFC-11 and CFC-12 saturations decrease dramatically to less than 60%, due to mixing near the front [Sloyan et al., 2010]. The 60% saturation for AAIW in late winter north of the SAF is similar to that observed for recently formed Labrador Sea Water in 1500 m mixed layers, though formation mechanisms are somewhat different [Wallace and Lazier, 1988; Rhein et al., 2002].

**Figure 2.3:** a) Colored contour represents CFC-12 surface saturations (%) relative to the 2005 atmosphere from the 2005 data. Black contours represent density in kg m\(^{-3}\), and white contours are potential temperature in \(^{\circ}\)C. The approximate location of the SAF during the 2005 cruise is along the 4\(^{\circ}\)C isotherm. b) Colored contours represent CFC-12 saturations along 27.2 kg m\(^{-3}\) (the core of AAIW). White contours are the depth of the 27.2 kg m\(^{-3}\) isopycnal. The approximate location of the SAF during the 2005 cruise is along the 600 m contour. Note the change in CFC-12 saturations poleward and equatorward of the SAF. There is a scale change between a and b.
2.4 CFC-12 inventories

CFC-12 inventories were calculated for SAMW and AAIW using a technique described in earlier work [Orsi et al., 1999; Smethie and Fine, 2001; Rhein et al., 2002; LeBel et al., 2008] :

\[ CFC_{\text{inv}} = \rho \sum \left[ [CFC]_{(ij)} \cdot A \cdot D_{(ij)} \right] \]  

(2.1)

where \( CFC_{\text{inv}} \) is the CFC-12 inventory in moles, \( \rho \) is the density of water (kg m\(^{-3}\)), \([CFC]_{(ij)}\) is the CFC-12 concentration (pmol kg\(^{-1}\)) at latitude \((i)\) and longitude \((j)\), \( A \) (m\(^2\)) is the area of the grid box (2.5°x5°, from Willey et al., 2004), and \( D_{(ij)} \) (m) is the thickness of each layer (SAMW or AAIW) at a location \( i \) and \( j \). The inventories for SAMW (26.80 - 27.06 kg m\(^{-3}\)) are calculated between the SAF and the equator, and for AAIW (27.06-27.40 kg m\(^{-3}\)), from the PF to 20°N. The boundaries for both SAMW and AAIW extend from 150°E to 70°W. Temperature, salinity, and density data along each meridional WOCE and CLIVAR section were analyzed to determine if the location of the SAF and PF are significantly different than the climatological mean location from Orsi et al. [1995]. The only significant difference was along 170°W, where the location of the PF was approximately 5° north of the Orsi et al. (1995) mean. Stations located south of the SAF for SAMW and south of the PF for AAIW are not included in the inventory calculations.

The total CFC-12 normalized inventory (see section 2.4.1 for normalization technique) for SAMW between 26.80 and 27.06 kg m\(^{-3}\) is 16.0.0x10\(^6\) moles. The total inventory for AAIW between 27.06 and 27.40 kg m\(^{-3}\) is 8.7x10 \(^6\) moles. The inventory map (Figure 2.4a) is smoothed based on a two dimensional running mean of the gridded CFC-12 inventories within SAMW. The technique reduces the CFC-12 inventory
maxima. Therefore, the maximum CFC-12 inventories at a hydrographic station are 4.6 moles km$^{-2}$ within the original data, 2.0 moles km$^{-2}$ within the gridded data, and 0.77 moles km$^{-2}$ within the two dimensional smoothed data.

**Figure 2.4:** CFC-12 inventory maps normalized to 2005 in mol km$^{-2}$ for a) SAMW from the SAF to the equator and, b) AAIW, from the PF to 20°N. White dashed line is the mean location of the SAF and the white solid line is the mean location of the PF from Orsi et al. (1995).
The smoothed data are used, as they provide a more continuous average picture of the CFC-12 inventories extrema over the South Pacific. As with SAMW, the AAIW inventory map (Figure 2.4b) is smoothed both in latitude and longitude. The maximum CFC-12 inventories are 4.0 moles km\(^{-2}\) in the original data, 1.6 moles km\(^{-2}\) in the gridded data, and 0.79 moles km\(^{-2}\) in the gridded two dimensional smoothed data. The total CFC-12 inventories for SAMW and AAIW vary by < 1% when using the smoothed or unsmoothed data.

### 2.4.1 Normalization of CFC inventories to the year 2005

The distribution of CFC data within the South Pacific spans 17 years, from 1989 to 2006. This presents a challenge in calculating a CFC inventory relative to a given date, as the atmospheric CFC concentrations vary with time [Walker et al., 2000]. Therefore, the inventories at each station were normalized to a constant date in order to obtain a quasi-synoptic inventory of CFC-12. A constant date of January 1, 2005 was chosen because SAMFLOC data were collected in the austral winter of 2005. The technique used is similar to Smethie et al. [2000], where CFC-12 inventories at each station are scaled by a normalization factor.

In order to investigate the basin-wide circulation of SAMW and AAIW, pCFC-12 age maps along the core of each water mass were constructed (Figure 2.5a and b). The age of the water masses were calculated at each hydrographic location within the South Pacific using the partial pressure (pCFC) method from Fine et al. [1988] and Doney and Bullister[1992]:

\[
pCFC = \frac{[CFC]}{F(\theta, S, sat)} \quad (2.2)
\]
where [CFC] is the measured CFC-12 concentration in seawater, and F is the solubility from Warner and Weiss (1992) based on potential temperature (θ) and salinity (S), and sat, the saturation of CFC-12 at the formation region from the 2005 data. The equation does not take into account the path of the water parcel. The assumption is that the temperature and salinity do not change once leaving the formation region (see section 2.6 for error analysis). The pCFC is compared to the atmospheric history to obtain a year of formation [Walker et al., 2000]. This year of formation is then subtracted from present day to determine the age of the water mass. When the CFC-12 concentrations are < 0.02 pmol kg⁻¹, ages were not calculated due to the large errors at these low concentrations [Smethie et al., 2000].

![Figure 2.5](image.jpg)

**Figure 2.5:** CFC-12 relic age maps in years a) for SAMW and b) for AAIW. The dashed line in panel a is the location of the SAF and the dashed line in panel b is the location of the PF.
Typically the pCFC age at the region of formation is not zero due to mixing, dilution, and entrainment of older waters during formation. The non-zero formation age is known as the relic age of the water mass [e.g. Fine et al., 2002] and is subtracted from the pCFC age to properly account for water mass formation processes that cause undersaturation of CFC-12 in newly formed water masses. In this study, relic ages for SAMW and AAIW are 10 years and 15 years, respectively, estimated from the winter 2005 SAMFLOC data. The relic age of AAIW is greater than that of SAMW due to more significant mixing and entrainment of lower CFC-12 concentration waters as AAIW subducts at the SAF (Figure 2.3b).

The relic corrected pCFC-12 ages are fairly zonal, with the youngest waters close to the source and progressively aging as distance from the source increases. This pattern allows for division of the South Pacific into seven meridional domains, in which the average annual percent change ($p_c$) for the year of formation is calculated over each domain. In other words, $p_c$ is the amount the atmospheric CFC-12 changed in one year compared to the previous year:

$$p_c = \frac{(atm_2 - atm_1)}{atm_1} \times 100 \quad (2.3)$$

where $atm_2$ is the atmospheric concentration of the year of formation (Eq. 2), and $atm_1$ is the atmospheric concentration of the previous year. The $p_c$ is then used in the calculation of the normalization factors.

Normalization factors ($N_f$) are calculated using:

$$N_f = (Y_{2005} - Y_d) \cdot p_c \quad (2.4)$$
where \( Y_{2005} \) is the chosen constant date of 2005, \( Y_d \) is the date of the hydrographic cruise, and \( p_c \) is the annual atmospheric percent change for the year the water mass was formed (Eq. 3) averaged over each domain. CFC-12 inventories at each station for SAMW and AAIW were normalized specifically to each cruise, rather than averaged. Data collected within one year of 2005 were not normalized. In principle, we modify the CFC data to become quasi-synoptic, as if they all were collected in 2005. As a check on the normalization process, inventories were also normalized to 1992. 1992 was the year with the most WOCE cruises over the South Pacific. Inventory patterns are similar using normalized data of 1992 (not shown) and 2005. Table 2.2 contains the average normalization factor within each domain, as well as the range of normalization factors.

<table>
<thead>
<tr>
<th>Latitude</th>
<th>Longitude</th>
<th>SAMW average normalization factor</th>
<th>Range of normalization factors for SAMW</th>
<th>AAIW average normalization factor</th>
<th>Range of normalization factors for AAIW</th>
</tr>
</thead>
<tbody>
<tr>
<td>64-54°S</td>
<td>75°W-150°E</td>
<td>1.06</td>
<td>1.05-1.07</td>
<td>1.14</td>
<td>1.11-1.15</td>
</tr>
<tr>
<td>54-45°S</td>
<td>75°W-150°E</td>
<td>1.15</td>
<td>1.12-1.16</td>
<td>1.25</td>
<td>1.19-1.26</td>
</tr>
<tr>
<td>45-36°S</td>
<td>75°W-150°E</td>
<td>1.45</td>
<td>1.36-1.54</td>
<td>1.60</td>
<td>1.48-1.73</td>
</tr>
<tr>
<td>36-27°S</td>
<td>75°W-150°E</td>
<td>1.77</td>
<td>1.55-1.84</td>
<td>1.90</td>
<td>1.66-1.99</td>
</tr>
<tr>
<td>27-18°S</td>
<td>75°W-150°E</td>
<td>2.01</td>
<td>1.78-2.19</td>
<td>2.05</td>
<td>1.81-2.23</td>
</tr>
<tr>
<td>18-0°S</td>
<td>75°W-150°E</td>
<td>2.31</td>
<td>2.04-2.60</td>
<td>2.17</td>
<td>1.07-2.43</td>
</tr>
<tr>
<td>0-20°N</td>
<td>75°W-150°E</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2.2: Average normalization factors and range of normalization factors over the inventory domains for SAMW and AAIW. Each hydrographic station has its own factor based on time of cruise and relic age of water at that location.

2.5 Water mass formation rates

Average water mass formation rates over the period of CFC input, mostly since 1970, are calculated based on [Smethie and Fine, 2001; Kieke et al., 2006; LeBel et al., 2008]:

\[
R = \frac{\int_0^{CFC_{inv}} \rho_{CFC} (C_s(t) - sat) dt}{\int_0^{t_{N}} \rho_{CFC} (C_s(t) - sat) dt} \quad (2.5)
\]
where $CFC_{inv}$ is the normalized CFC-12 inventory from 2005 in moles, $\rho$ is the density of water (kg m$^{-3}$), $C_s(t)$ (pmol kg$^{-1}$) is the CFC-12 concentration at the source at 100% equilibrium with the atmosphere for the years 1970 to 2005, and $sat$ is the percent CFC-12 saturation at the source, 95% and 60% for SAMW and AAIW, respectively. The assumptions are that the percent saturation at the time of formation and the formation rate are constant over the period of CFC input (see section 5.3 for a discussion of errors associated with this assumption).

Based on this inventory, the water mass formation rate for SAMW remaining within the South Pacific is 7.3 Sv ± 2.1 Sv ($1$ Sv = $10^6$ m$^3$ s$^{-1}$). The formation rate for AAIW is 5.8 Sv ± 1.7 Sv (see section 6 for error analysis). These rates represent the average formation rates for SAMW and AAIW within the South Pacific over the major period of CFC input from 1970 to 2005.

One potential influence on the formation rates not included is obduction. Obduction is the transfer of water from the permanent thermocline to the mixed layer above [Qiu and Huang, 1995]. The process of obduction may affect the CFC saturation, influencing the inventories and formation rates. A flux of older water from the permanent thermocline into the mixed layer would result in CFC saturations significantly out of equilibrium with the present atmosphere. From the 2005 winter data, we find that within the mixed layers, CFC and oxygen saturations are close to equilibrium in the density range of SAMW and AAIW (section 2.3). Thus, we assume that the effect of obduction on the CFC saturations is small.

There are regions of potential CFC loss from the layers of SAMW and AAIW and from the South Pacific. CFC concentrations are decreased within the layers of SAMW
and AAIW by vertical mixing. While we cannot directly quantify this loss, observations show that CFC concentrations are at or close to zero below AAIW. Similarly, on SAMW and AAIW isopycnals in the Pacific subtropical gyre, CFC-12 concentrations are at or close to zero, northwest of 30°S, 160°E (not shown). These observations suggest that there is a minimal transfer of CFC-12 to the layers below and to the Indian Ocean via the Indonesian Throughflow. Furthermore, if concentrations of CFC-12 are near zero and are being mixed to layers below, these losses are insignificant to our inventory and formation rate calculations.

The total formation rate of SAMW and AAIW in the South Pacific additionally includes the portions that exit to the Atlantic Ocean through the Drake Passage \cite{McCartney1977,McCartney1982,Talley1996}. To estimate the formation rates, we calculated volume transports along our winter 2005 77°W section from 55°S to 61°S, within the SAMW and AAIW layers. The meridian 77°W was chosen because it is the closest hydrographic section to the Drake Passage. Geostrophic transports were calculated relative to the bottom. We estimate that 4.4 Sv ± 0.6 Sv of SAMW was transported across 77°W, comparable to the 4.8 Sv ± 0.5 Sv reported by Sloyan and Rintoul \cite{Sloyan2001b} using an inverse model and an independent data set. Combining the formation rate of SAMW based on the CFC-12 inventory in the South Pacific subtropical gyre of 7.3 Sv ± 2.1 Sv with the geostrophic transport across 77°W of 4.4 Sv ± 0.6 Sv gives an average of 11.7 Sv ± 2.2 Sv (see section 2.6 for a full analysis of errors) of SAMW that is inferred to be forming in the southeast Pacific.

A total of 19.8 Sv ± 2.0 Sv of AAIW was transported across 77°W in 2005, relative to the bottom. As AAIW is a small part of the large transport of the Subantarctic
Zone, it is difficult to quantify how much newly formed AAIW is being transported through the Drake Passage. There is significant circumpolar-circulated AAIW within the ACC as well as recirculation of AAIW southward along the Chilean coast [Koshlyakov and Tarakanov, 2005]. Thus, for AAIW we consider the 5.8 Sv ± 1.7 Sv calculated from the South Pacific CFC inventory as a lower bound on the rate of AAIW formed in the southeast Pacific.

Error estimates on the transports are derived from Firing et al. [2011]. They find a mean transport of 95 Sv with a standard deviation of 10 Sv from 51 direct velocity transects of the upper 1000 m of the Drake Passage, made over a period of 4.5 years. We estimate a total of 24.2 Sv (4.4 Sv + 19.8 Sv) of SAMW and AAIW transported across 77°W. We scaled the standard deviation reported by Firing et al. (2011) by the transport ratio (24.2/95), assuming the error is distributed proportionately, to estimate an error of ± 2.5 Sv on the transports across 77°W. Our SAMW/AAIW transport estimate likely underestimates the transport because it is only the baroclinic component. However, since the error estimate is based on direct velocity observations, it included both barotropic and baroclinic variability. Also, the error may overestimate variability in the SAMW/AAIW transport, as the Firing et al. (2011) study included surface waters.

There are a few studies that have looked at the total transport of SAMW and AAIW within the Drake Passage. Cunningham et al. [2003] find approximately 36 Sv ± 2.7 Sv of SAMW and AAIW based on a series of sections within the Drake Passage from 1993 to 2000. Naveira Garabato et al. [2003] uses an inverse model across multiple sections within the Drake Passage and finds approximately 28 Sv ± 2.5 of SAMW and AAIW. Our transport is close to that found in Naveira Garabato et al. (2003) but it is
considerably less than the Cunningham et al. (2003) transport. Transports of SAMW and AAIW may increase once within the Drake Passage due to diapycnal diffusion; this was shown for AAIW in Naveira Garabato et al. (2003). We can see from these three studies that variability in the transport of SAMW and AAIW through the Drake Passage is small. This error estimate helps support our conclusion that 11.7 Sv ± 2.2 Sv for SAMW is an average formation rate.

2.6 Error analysis

The error analysis follows that of LeBel et al. [2008]. Significant errors in the formation rates result from three sources: errors related to CFC input, errors on the integrated inventories and their normalization to a constant date, and errors associated with assuming a constant formation rate over the period of the CFC input.

2.6.1 CFC input and solubility

The errors related to the CFC atmospheric source are due to the uncertainties in the atmospheric time history of the CFCs, and the uncertainties related to the solubility of CFCs. Atmospheric time history errors are considered less than 1% after 1970 [Walker et al., 2000]. The solubility of CFCs as a function of temperature and salinity is well known from laboratory measurements [Warner and Weiss, 1985]. A change in temperature after leaving the formation region, which has the most effect on solubility, of 1-2°C results in approximately 4-6% uncertainty in the solubility (Eq. 2). Within the South Pacific, SAMW and AAIW change by approximately 1-2°C between ~60°S and 20°S.
2.6.2 Integrated CFC inventories and time normalization

The sources of error in the CFC inventories are from measurement errors on individual seawater samples, errors due to normalizing data to a constant date, and errors due to limited spatial coverage. The measurement errors on individual samples are less than 2%, which propagates through the vertical integration to approximately 2% [Smethie and Fine, 2001]. Errors from normalizing the data are estimated by comparing the CFC-12 concentrations of the normalized data to the original data from the occupations of P16, along 150°W, in 1991-1992 and in 2005-2006. The total average errors due to normalizing CFC-12 to a constant date are approximately 20% for both SAMW and AAIW.

Lastly, there are the errors associated with the spatial integration of the interpolated CFC-12 inventories. Regions of less dense sampling and of large CFC gradients will generate the most error in the CFC inventories [e.g. Waugh and Abraham, 2008]. A bootstrap method is used in which 50% of the inventory data are randomly selected 100 times, gridded, and the root mean square variability (rms) is calculated for each grid point [Rhein et al., 2002; Kieke et al., 2006; LeBel et al., 2008]. The resulting rms is a measure of the degree of uncertainty in the CFC-12 inventory due to the combined effects of the errors, non-synopticity of the cruises, large gradients in the data, and the spatial resolution of the data. The errors are 3% for SAMW and 6% for AAIW. Larger errors are associated with AAIW possibly due to stronger gradients in AAIW. These errors are the most conservative estimates, as they are based on the largest rms values.
2.6.3 Constant formation rate

In applying the CFC inventory method, percent saturation and formation rates are assumed to be constant over the time of CFC input, 1970s to 2005. LeBel et al. [2008] and Smethie and Fine [2001] carried out elaborate sensitivity studies on Labrador Sea Water (LSW) to address this. While there is very well documented variability within LSW [Dickson et al., 1996; Lazier et al., 2002], there is only limited information on the variability of SAMW and AAIW.

Between 1993 and 2004, the South Pacific subtropical gyre wind-driven circulation increased by at least 20% (Roemmich et al., 2007). The increase in gyre circulation is attributed to an increase in the Southern Annular Mode (SAM) from 1990 to 1999, with a peak in 1998. During a positive SAM, subpolar westerlies increase with a resulting increase in the northward Ekman transport, as well as a global asymmetric deepening of the mixed layers affecting SAMW and AAIW [Hall and Visbeck, 2002; Naveira Garabato et al., 2009; Sallee et al., 2010].

In this study, we use the Roemmich et al. (2007) circulation as an example of the potential effects of the SAM on intermediate water circulation and formation rates. We assume that a change in the wind forcing, along with a change in the mixed layer depth, will affect the formation of SAMW and AAIW, although we acknowledge that formation changes may not be uniform across the South Pacific [Sallee et al., 2010]. A sensitivity study is carried out to estimate the change in formation rates for SAMW and AAIW based on changes in the SAM. For lack of a better number, we used 20% from the Roemmich et al. (2007) circulation study and varied the formation rates over the SAM index [Marshall, 2003]. We assume a linear response between SAM and the formation
of SAMW and AAIW with no lag between the forcing and the response of SAMW and AAIW. The resulting formation rate for SAMW could then vary between 14.0 Sv (2003) to 9.4 Sv. For AAIW, the formation rate could vary between 7.0 Sv (2003) to 4.6 Sv.

2.6.4 Total error

The total error in the formation rates for SAMW and AAIW is calculated by combining the errors in CFC input and solubility, CFC inventories and normalization, and the assumption of constant formation rate. The errors are combined as the square root of the sum of the errors [Wolberg, 1967]. These terms contribute a total error of 29% for SAMW and 30% for AAIW. The errors represent the most conservative estimates for the formation rates presented here.

2.7 Discussion

2.7.1 SAMW and AAIW formation areas

A map of the SAMW CFC-12 inventory (Figure 2.4a) shows there are two areas of relative maxima (>0.6 moles km$^{-2}$), one centered on 90°W and the other centered on 150°W. We interpret these maxima as evidence of two main areas of SAMW formation in the Pacific sector of the Southern Ocean, consistent with the findings of McCartney [1982]. Winter mixed layer depths greater than 400 m, equatorward of the SAF, are associated with each area [Holte et al., 2012]. In the Pacific the highest inventory of SAMW is centered on 90°W. This is visible from the inventory map with a large area of greater than 0.8 moles km$^{-2}$ (Figure 2.4a).

The second high CFC-12 inventory lies between about 170°W and 130°W, it is greater than 0.6 moles km$^{-2}$. A high inventory there is consistent with the findings in
Sallee et al. [2010] of a new area of SAMW formation over the Eltanin Fracture Zone (140°W). There is also a small area of high CFC-12 inventory for SAMW, poleward of New Zealand. Sallee et al. (2010a) find this is a formation area for SAMW that is driven by subduction within mixed layers along the Campbell Plateau. However, Sallee et al. (2010a) do not find any evidence of formation of SAMW in the southeast Pacific, where this study finds the greatest Pacific inventory of CFC-12.

CFC-12 inventory maxima (>0.7 mol km$^{-2}$) for AAIW also lie within the southeast Pacific (100°W), poleward of SAMW (Figure 2.4b). They are associated with low salinity at potential densities greater than 27.06 $\sigma_T$, and are located south of the SAF. The maximum in the AAIW inventory in the southeast Pacific is consistent with previous findings [Iudicone et al., 2007], which report that the main site of AAIW formation is the southeast Pacific followed by AAIW transport into the subtropical gyres of both the Atlantic and Pacific.

For both SAMW and AAIW, more than 98% of the total CFC-12 inventory still remains poleward of 30°S. This high percentage is due to the significant uptake of gases near the fronts associated with the ACC and within the deep winter mixed layers. The substantial decrease equatorward of the maximum inventories is due to mixing with depleted CFC waters as SAMW and AAIW are transported northward from the fronts.

2.7.2 Mesoscale eddy influence on SAMW and AAIW formation

Within the original (non-gridded) inventories of SAMW and AAIW along 170°W and 150°W there are stations of higher than average CFC-12 inventories. Upon close investigation of the hydrographic data and satellite images from the time of the 170°W cruise in 1996 and the 150°W cruise in 2005, these CFC-12 inventory maxima appear to
be coincident with eddies. Hydrographic data, such as temperature, salinity, and density along the sections, suggest that these eddies are approximately two degrees in diameter. The properties within these eddies are similar to those found within SAMW and AAIW in the high CFC-12 inventories further to the east.

Between 170°W and 150°W, there were multiple cyclonic and anticyclonic eddies observed in 1996 and 2005. The cyclonic cold-core eddies are enriched in CFC concentrations (Figure 2.6). Originating from the south, they apparently transport cold, gas enriched waters equatorward to influence properties of SAMW, as also observed south of Tasmania [Morrow et al., 2004; Herraiz-Borreguero and Rintoul, 2010]. The anticyclonic eddies have the potential to be sites where CFCs are added through air-sea modification similar to what was observed south of Africa by Olson et al.[1992]. In addition, in the Subantarctic Zone, the East Australian Current (EAC) is a source of warm and salty anticyclonic eddies influencing SAMW properties [Ridgway and Dunn, 2007]. The Southern Ocean, and in particular the fronts associated with the ACC, are dominated by eddies, especially along 170°W, the Campbell Plateau, and the Australian sector of the Southern Ocean [e.g. Olson and Emery, 1978; Gille et al., 2000; Phillips and Rintoul, 2000]. Eddies play a critical role in the stratification and circulation of the Southern Ocean, and have been shown to affect tracer and CO₂ distributions, as well as the formation of AAIW [e.g. Lachkar et al., 2007]. Therefore, depending on the number of eddies shed per year by the ACC, the EAC, and due to the influence of the Campbell Plateau, eddies could be making a significant contribution to the formation and properties of SAMW and to a lesser extent AAIW. A rough calculation of removing two to three CFC-12 enriched eddies from the inventory calculation decreased by approximate 5% the
total inventory, or each eddy decreased the inventory by about 2% and approximately 0.1 Sv change in the formation rate. The tracer method of CFC-12 inventories and formation rate calculations presented here take into account all formation mechanisms contributing to SAMW and AAIW, including eddy processes.

![Figure 2.6: Depth section along 170°W of CFC-12 concentrations in pmol kg⁻¹. Black contours represent potential density in kg m⁻³. Cold core eddies centered around 51°S and 47°S. Note the high CFC-12 concentration within these eddies extending into SAMW density surfaces (26.8 - 27.06 kg m⁻³).](image)

### 2.7.3 Global comparison of mode and intermediate waters

SAMW and AAIW are an integral part of the global overturning circulation. They are formed at specific sites in the Southern Ocean and modified within each of the Atlantic, Indian, and Pacific Oceans and transported between the three oceans.

A few observational and model studies have attempted to calculate formation rates for SAMW and AAIW within the South Pacific. For a more complete comparison with other work see Table 2.3. Considering the substantial differences in chosen density layers used by each study, the closest comparison can be made for SAMW with that of Qu et al. [2008]. Qu et al. (2008) use high resolution CTD and ARGO profiles of differences in winter mixed layer depths to calculate an annual subduction rate for the SAMW. In the South Pacific, they estimate approximately 11.6 Sv of SAMW is formed,
and this compares very well to our value of $11.7 \text{ Sv} \pm 2.2 \text{ Sv}$. Since the calculation of Qu et al. (2008) misses much of the lower part of AAIW, the closest comparison for AAIW is with that of Sloyan and Rintoul (2001b). Sloyan and Rintoul (2001b) calculate formation rates based on inverse methods for AAIW of 4.5 Sv, compared to our value of at least $5.8 \text{ Sv} \pm 1.7 \text{ Sv}$. Thus, these recent estimates for formation of SAMW and AAIW in the South Pacific that use physical parameters are in good agreement with the CFC-12 inventory method presented here.

SAMW and AAIW are also formed in the South Atlantic and Indian Oceans. Karstensen and Quadfasel [2002] estimate approximately 9-10 Sv of mode and intermediate waters subducted in the South Atlantic. Sloyan and Rintoul (2001b) estimate 8.4 Sv of AASW transformed into SAMW in the South Atlantic. As for the Indian Ocean, Sallee et al. (2010a) find approximately 4 Sv of less dense SAMW formed just in the southeast Indian Ocean. Sloyan and Rintoul (2001b) estimate 16 Sv of SAMW and 6.6 Sv of AAIW formed within the Indian Ocean. Karstensen and Quadfasel [2002] estimate approximately 22 Sv of mode water subducting in the Indian Ocean. Based on these estimates it appears that the formation of $17.5 \text{ Sv} \left(11.7 + \text{ at least } 5.8 \text{ Sv}\right)$ of SAMW and AAIW within the South Pacific is greater than that formed in the Atlantic. It also appears the SAMW formation within the Indian Ocean is greater than that of the Pacific Ocean. However, the volume of the mode water layer within both the Karstensen and Quadfasel (2002) and Sloyan and Rintoul (2001b) studies is thicker and extends higher into the water column than in the Pacific. When looking at only the densest mode waters in the Indian Ocean from Karstensen and Quadfasel (2002), comparable to that of the
South Pacific, the formation of SAMW in the South Pacific is greater than that of the Indian Ocean (~7 Sv).

How do the formation rates in this study of SAMW and AAIW compare with rates of formation of northern hemisphere mode and intermediate waters (Table 2.3)? In the North Atlantic, Labrador Sea Water (LSW) has been observed to form in as deep as 1500m mixed layers. Using the CFC inventory method to estimate formation rates, LSW formation rates range from 7 Sv to 12 Sv and the formation is known to vary over time [Smethie and Fine, 2001; Rhein et al., 2002; Kieke et al., 2006; LeBel et al., 2008]. For years with convection, LSW rates are comparable to our total SAMW formation rate of 11.7 Sv ± 2.2 Sv and greater than the 5.8 Sv ± 1.7 Sv lower bound estimate for AAIW formed in the southeast Pacific.

Within the North Pacific, SAMW is compared with Central Mode Water (CMW). CMW is formed via similar circumstances as SAMW, within winter mixed layers, and is characterized by a low in potential vorticity [Oka and Suga, 2005]. SAMW formation rate is greater than CMW, 11.7 Sv ± 2.2 Sv for total SAMW and 7.6 Sv for CMW from an isopycnel model [Ladd and Thompson, 2001]. North Pacific Intermediate Water (NPIW), like AAIW is characterized by a salinity minimum. Wong et al. [1998], estimates a minimum of 2.7 Sv of NPIW forming in the Okhotsk Sea. This NPIW estimate is smaller than our estimate of AAIW in the South Pacific, and this is not surprising when the CFC distributions of the two water masses are compared (Fine et al., 2001).

Total SAMW and AAIW formation rates for the South Pacific are comparable to the formation rate of LSW, and are greater than the formation rates of CMW and NPIW.
<table>
<thead>
<tr>
<th>Water Mass</th>
<th>Formation Rate</th>
<th>Author</th>
<th>Method</th>
<th>Density (kg m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAMW</td>
<td>11.7 Sv</td>
<td>This work</td>
<td>CFC-12 inventory + geostrophic transports</td>
<td>26.80-27.06</td>
</tr>
<tr>
<td></td>
<td>9 Sv</td>
<td>Fine et al. (2001)</td>
<td>CFC ages</td>
<td>26.5-27.1</td>
</tr>
<tr>
<td></td>
<td>11.6 Sv</td>
<td>Qu et al. (2008)</td>
<td>annual subduction rate</td>
<td>26.8-27.1</td>
</tr>
<tr>
<td></td>
<td>11 Sv</td>
<td>Marsh et al. (2000)</td>
<td>MICOM model</td>
<td>26.5-27.2</td>
</tr>
<tr>
<td></td>
<td>7 Sv</td>
<td>Speer et al. (1997)</td>
<td>air-sea flux estimates</td>
<td>*27.0 (\gamma^n)</td>
</tr>
<tr>
<td></td>
<td>11.4 Sv</td>
<td>Sloyan and Rintoul (2001b)</td>
<td>Inverse methods</td>
<td>*26.0-27.0 (\gamma^n)</td>
</tr>
<tr>
<td></td>
<td>10.0 Sv</td>
<td>Macdonald et al. (2009)</td>
<td>Inverse methods</td>
<td>*26.2-27.1 (\gamma^n)</td>
</tr>
<tr>
<td></td>
<td>7 Sv</td>
<td>Sallee et al. (2010)</td>
<td>annual subduction rate</td>
<td>26.8-27.0</td>
</tr>
<tr>
<td>AAIW</td>
<td>5.8 Sv</td>
<td>This work</td>
<td>CFC-12 inventory</td>
<td>27.06-27.40</td>
</tr>
<tr>
<td></td>
<td>8 Sv</td>
<td>Fine et al. (2001)</td>
<td>CFC ages</td>
<td>27.1-27.3</td>
</tr>
<tr>
<td></td>
<td>8.5 Sv</td>
<td>Marsh et al. (2000)</td>
<td>MICOM model</td>
<td>27.2-27.5</td>
</tr>
<tr>
<td></td>
<td>4.5 Sv</td>
<td>Sloyan and Rintoul (2001b)</td>
<td>Inverse methods</td>
<td>*27.0-27.4 (\gamma^n)</td>
</tr>
<tr>
<td></td>
<td>10.0 Sv</td>
<td>Macdonald et al. (2009)</td>
<td>Inverse methods</td>
<td>*27.1-27.6 (\gamma^n)</td>
</tr>
<tr>
<td></td>
<td>4 Sv</td>
<td>Sallee et al. (2010)</td>
<td>annual subduction rate</td>
<td>27.1-27.2</td>
</tr>
<tr>
<td>LSW</td>
<td>7-12 Sv</td>
<td>Rhein et al. (2002); Kieke et al. (2006); LeBel et al. (2008)</td>
<td>North Atlantic</td>
<td></td>
</tr>
<tr>
<td>SAMW+AADIW</td>
<td>9-10 Sv</td>
<td>Karstensen and Quadfasel (2002)</td>
<td>South Atlantic</td>
<td></td>
</tr>
<tr>
<td>CMW</td>
<td>7.6 Sv</td>
<td>[Ladd and Thompson, 2001])</td>
<td>North Pacific</td>
<td></td>
</tr>
<tr>
<td>NPIW</td>
<td>2.7 Sv</td>
<td>Wong et al. ([1998])</td>
<td>North Pacific</td>
<td></td>
</tr>
<tr>
<td>SAMW</td>
<td>4 Sv</td>
<td>Sallee et al. (2010)</td>
<td>Indian</td>
<td></td>
</tr>
<tr>
<td>SAMW</td>
<td>16 Sv</td>
<td>Sloyan and Rintoul (2001b)</td>
<td>Indian</td>
<td></td>
</tr>
<tr>
<td>SAMW+AADIW</td>
<td>22 Sv</td>
<td>Karstensen and Quadfasel (2002)</td>
<td>Indian</td>
<td></td>
</tr>
<tr>
<td>AAIW</td>
<td>6.6 Sv</td>
<td>Sloyan and Rintoul (2001b)</td>
<td>Indian</td>
<td></td>
</tr>
</tbody>
</table>

* density is in neutral density rather than sigma-theta.

**Table 2.3:** Comparison of mode and intermediate water formation rates within the literature. SAMW, Subantarctic Mode Water, AAIW, Antarctic Intermediate Water, LSW, Labrador Sea Water, CMW, Central Mode Water, NPIW, North Pacific Intermediate Water.

SAMW and AAIW formation in the South Pacific are also greater than the formation within the Indian and Atlantic Oceans for intermediate densities. Therefore, SAMW and AAIW formed in the South Pacific make a significant contribution to the overall global
formation and circulation of mode and intermediate waters. The properties of SAMW and AAIW formed in the South Pacific influence SAMW and AAIW properties within the southern hemisphere subtropical gyres. Their properties also influence global and low latitude biological export production [i.e. Marinov et al., 2006; Roemmich et al., 2007; Naveira Garabato et al., 2009].

2.8 Summary and conclusions

SAMW and AAIW influence the capacity of the southern hemisphere subtropical gyres to store climatologically important properties such as, heat, freshwater, and CO₂. This study presents the first wintertime observations of CFC-11 and CFC-12 saturations within SAMW (94% and 95%) and AAIW (60%, north of the SAF) within the southeast Pacific. Accurate knowledge of these winter mixed layer saturations enables the robust calculation of CFC-12 inventories within SAMW and AAIW. The CFC-12 inventory maps provide a basin-wide picture of the areas of formation of SAMW and AAIW. In the Pacific sector of the Southern Ocean the primary region of formation of SAMW and AAIW is the southeast Pacific. The inventory maps provide direct evidence that SAMW also has another major area of formation in the central Pacific, as proposed by McCartney (1982). Higher CFC-12 inventories in eddies in the central Pacific are suggestive of higher local formation rates for SAMW, and to a lesser extent for AAIW. The CFC-12 inventories are used to calculate formation rates for SAMW at 7.3 Sv ± 2.1 Sv and 5.8 Sv ± 1.7Sv for AAIW that circulate within the South Pacific subtropical gyre. Based on a transport of 4.4 Sv from the South Pacific through the Drake Passage, the total formation rate of SAMW in the South Pacific is 11.7 Sv ± 2.2 Sv. The AAIW formation rate of 5.8 Sv± 1.7 Sv is a lower bound on the formation of AAIW within the South Pacific, as we
cannot estimate the volume transport of newly formed AAIW through the Drake Passage. The CFC-derived formation rates represent the average water mass formation rates over the period from 1970 to 2005, and take into account all formation processes, including eddies, winter convection, and mixing. SAMW and AAIW formation in the South Pacific represent a major portion of the mode and intermediate water formation worldwide. This study provides a multi-decadal average of SAMW and AAIW formation rates, providing a baseline with which to compare past and future formation rates of SAMW and AAIW.
Chapter 3

Chlorofluorocarbon Analysis of the Southern Hemisphere Oceans in NCAR-CCSM4

3.1 Introductory remarks

This work was performed as a part of a large collaborative project looking at the Southern Ocean components in CCSM4. This work is published in Weijer et al, [2012], entitled The Southern Ocean and its Climate in CCSM4.

Chlorofluorocarbons (CFC-11 and CFC-12) are oceanic tracers that are used to evaluate circulation patterns, ages, and formation rates of water masses [e.g., Fine, 2011], and are a direct analogue to the physical processes of uptake and storage of CO$_2$ in the oceans. CFCs are anthropogenic compounds that have been continuously added to the atmosphere since the 1930s. Concentrations have increased in the atmosphere up to the late 1990s for CFC-11 and to the early 2000s for CFC-12. The largest increase in concentrations in both the atmosphere and oceans occurred after the 1970s. CFCs enter the surface ocean from the atmosphere by gas exchange, with an average equilibration time of about 1 month [Broecker et al., 1980]. Once they become isolated from the atmosphere, CFC concentrations are stable in the ocean interior, except for the effects of mixing with waters of different concentrations. Global CFC oceanic observations were made starting in the 1980s and continued during the 1990s as a part of the World Ocean Circulation Experiment (WOCE) and in the 2000s as a part of Climate Variability and Predictability (CLIVAR). These programs have allowed for the direct comparison of
model CFC fields with these hydrographic observations. Here, the more soluble of the CFCs is used – CFC-11.

### 3.2 Model - observation comparison

In order to assess how the model is representing current ocean conditions, the CFC-11 distributions from observations and five model mean ensemble, at approximately the corresponding month, are compared in the South Pacific, 150°W (P16) (Figure 3.1 a and b). While surface CFC-11 concentrations are high due to air-sea flux, measureable CFC-11 waters ( > 0.05 pmol kg\(^{-1}\)) penetrate down to at least 1500 m between 55°S to 45°S.

![Figure 3.1: CFC-11 concentrations (pmole kg\(^{-1}\)) in the South Pacific along CLIVAR section P16 in 2005. a) Hydrographic observations and b) Ensemble mean from 2005.](image)
CFC-11 concentrations (the 0.5 pmol kg$^{-1}$ contour) gradually shoal from 35°S towards the equator, as density surfaces shoal. The monthly mean ensemble CFC-11 field in 2005 from the model, shows a similar pattern of the distribution of CFC-11 along 150°W. However, the CFC-11 distribution is shifted slightly shallower when compared to the observations, suggesting limited subduction along denser isopycnals. In the 2005 CFC observations, there is a small signature of Antarctic Bottom Water (AABW) extending from 70°S to 30°S, with above blank-level CFC-11 concentrations of > 0.01 pmol kg$^{-1}$. In the model, the 0.01 pmol kg$^{-1}$ contour, representing AABW does not extend as far.

**Figure 3.2:** CFC-11 concentration differences between the ensemble mean from 2005 simulations and observations in the South Pacific along CLIVAR section P16 in 2005. The black contours are the potential density surfaces from the model in kg m$^{-3}$. a) upper 2000m and b) 0-5000m.

equatorward as observed, suggesting limited formation of Pacific origin AABW within the model. However, global production of AABW in the Weddell and Ross Seas in the
model is within the range of observations [Danabasoglu et al., 2011]. Lastly, observed CFC-11 concentrations > 0.05 pmol kg\(^{-1}\) are found south of 65°S from the surface to approximately 500 m. In the model these higher concentrations are confined to above 300m.

Figure 3.3: CFC-11 concentration differences between the ensemble mean and observations in the South Pacific along WOCE section P16 in 1991/1992. The black contours are the potential density surfaces from the model in kg m\(^{-3}\). A) the upper 2000m and b) 0-5000m.

Differences amongst model and observations (model - observations) of CFC-11 concentrations along 150°W (P16) in the Pacific Ocean in 2005 show that CFC-11 in surface waters are generally higher in the model from 70°S to 45°S (Figure 3.2). Upper thermocline waters are higher within the model field compared to observations between about 35°S to 25°S above 500 m. Model CFC concentrations in the lower thermocline and intermediate waters, between the potential density surfaces of 26.5 and 27.5 kg m\(^{-3}\),
are significantly lower between 60°S and 20°S. South of 50°S (surface to 2000m), model CFC concentrations are over estimated, while bottom waters below 2000m are under estimated. A similar pattern is seen for the August of 1991 and October of 1992 reoccurrence of P16S, although the magnitude of the differences are smaller (Figure 3.3).

Model and data differences in the Indian Ocean are investigated along 90°E (I8/I9). This section was occupied in early 1995. As in the Pacific Ocean, the model Indian Ocean CFC-11 concentrations north of 45°, from the surface to intermediate

**Figure 3.4:** CFC-11 concentration differences between the ensemble mean and observations in the South Pacific along WOCE section A23 in 1995. The black contours are the potential density surfaces from the model in kg m⁻³. A) the upper 2000m and b) 0-5000m.

waters (27.5 kg m⁻³), are significantly lower compared with the observations (Figure 3.4 a and b). Surface waters between 65°S and 55°S have significantly higher CFC-11
concentrations in the model as compared with observations. Between 55°S and 30°S there are small and variable differences in surface concentrations. Model CFC-11 concentrations are lowest as compared with data among surface waters from 30°S to 20°S. Upper thermocline waters between 40°S and 20°S above 26.5 kg m$^{-3}$ are also lower within the model. Different from the Pacific Ocean, intermediate waters close to the outcrop region (55°S to 45°S) are slightly higher within the model, but then become lower downstream (45°S to 20°S). Another difference between the 1991 Pacific section and the 1995 Indian Ocean section are higher concentrations in the model from 65°S to 50°S, roughly extending to 1200 m. From 2000 m extending through the rest of the water

Figure 3.5: CFC-11 concentration differences between the ensemble mean and observations in the South Indian along WOCE section 18/19 in 1995. The black contours are the potential density surfaces from the model in kg m$^{-3}$. A) the upper 2000m and b) 0-5000m.
column, model deep waters are significantly lower in the Indian Ocean from 65°S to 45°S.

In the Atlantic Ocean we compare model and observation roughly along 30°W (A23), occupied in early 1995 (Figure 3.5 a and b). Model and observed surface water CFC-11 concentration differences vary across the section. Model CFC-11 concentrations between 70°S and 65°S and 50°S to 45°S are significantly higher. Upper thermocline waters, similar to the Indian Ocean are lower within the model fields. Model lower thermocline and intermediate waters, primarily between 26.5 and 27.5 kg m\(^{-3}\) have significantly lower CFC-11 concentrations from 45°S to 30°S. Just above 500 m, between 70°S and 45°S is a band of higher model CFC-11 concentrations. Different from

**Figure 3.6:** CFC-11 inventory (moles kg\(^{-2}\)) for section P16 in 2005 along 150°W. Red dots and stars are 0-500m from observations and model, respectively. Blue dots and stars are from 500-1500m and green dots and stars are from 1500-5000m.
the Indian and Pacific Ocean (in 2005), within the South Atlantic Ocean there are lower CFC-12 concentrations of both deep and bottom waters, from approximately 500 m down through the entire water column, from 70°S to about 40°S.

Another way to assess the model simulation of CFC-11 is to compare model and observed water mass CFC-11 inventories. This is done along P16 in 2005 (Figure 3.6). Focusing on the lower thermocline/intermediate waters at 55°S, the model CFC-11 inventories shift from higher than observations poleward of 55°S to lower than observations equatorward of 55°S. Lower model inventories along this section between 70°S and 60°S are the signature of the outcropping deep waters as seen in red in Figure 2. Equatorward of 55°S, the model CFC-11 inventories are low, which is also shown in concentrations in blue between densities 26.5 - 27.5 kg m\(^{-3}\) in Figure 3.2. These differences are greater than 0.25 pmol kg\(^{-1}\). Deep and bottom waters between 70°S and 55°S are significantly lower within the model by approximately 1 pmol kg\(^{-1}\). Surface water inventories vary across the section with the greatest discrepancy between the model and observations between 55°S to 35°S.

3.3 Discussion

Differences between the model CFC-11 field and the observations can shed light on the formation and ventilation of Southern Hemisphere water masses within the model. The largest differences between the model and observations across all three ocean basins are within the lower thermocline and intermediate waters. In these layers, the major water masses of the Southern Hemisphere are SAMW and AAIW. This suggests lower model CFC-11 concentrations of SAMW and AAIW or inadequate ventilation. The inadequate ventilation is strongest in the South Pacific and South Atlantic Oceans. This
inadequate ventilation is most likely caused by the parameterization of eddies within the model. The South Pacific makes up a major portion of the formation of intermediate water worldwide [Hartin et al., 2011]. Lower CFC-11 concentrations may have consequences for how other properties, such as heat, salt, CO$_2$ and nutrients are transported by the model. Focusing on the South Pacific, the higher model CFC-11 concentrations between 35°S and 25°S are likely due to the model over ventilating Subtropical Mode Water (STMW). Deep waters south of 50°S in all basins except the Atlantic are higher in CFC-11 concentrations. This may suggest less upwelling of CFC free Circumpolar Deep Water (CDW) within the model. Less CDW upwelling allows for the near-surface ocean build up of CFCs, which are not diluted by the CFC free CDW. Bottom waters in all three basins are lower in the model. Assuming that the model is adequately forming AABW [Danabasoglu et al., 2011], there is the possibility that there is too much mixing of AABW downstream with its surroundings.

As time into the CFC transient progresses, observations show that CFC-11 concentrations continue to increase in the water column as more waters are exposed to the atmosphere (not shown). Waters that are under ventilated in the model will be depleted in CFC-11 concentrations compared to observations, as observed in all basins within intermediate waters. Comparing P16 in the South Pacific from 1991 to P16 in 2005, these under ventilated waters in 1991 are now more depleted in CFC-11 in 2005. The opposite is true for the upper thermocline waters. These waters are over ventilated in 1991, and therefore in 2005, these waters have increased CFC-11 concentrations when compared to observations from 1991. To look at the model spread across the five ensemble members, the total water column inventory was calculated along each section.
The largest ensemble spread is between 70°S and 60°S (< 0.5 pmol kg⁻¹), where deep waters are outcropping at the surface (Figure 3.7a). Comparing 1991 and 2005 in the South Pacific, the ensemble spread increases in 2005 between 70°S and 60°S (> 0.5 pmol kg⁻¹) (Figure 3.7). The significant under ventilation of lower thermocline and intermediate waters (60°S to 40°S) is not due to variability within each run but rather a robust feature in all runs. These under estimations are not unique to the hydrographic sections chosen. The total water column CFC-11 inventory also shows the under estimation of lower thermocline and intermediate waters between 40°S and 60°S, when compared to the observations [Danabasoglu et al., 2011; figure 20].

**Figure 3.7:** CFC-11 inventory versus latitude across all ensemble members. P16 1991/1992 in stars and the reoccupation of P16 2005 in dots.

There are three main biases within the model that may play a role in the differences seen in CFC-11 concentrations; temperature, mixed layer depth, and wind stress. There is cold temperature bias within intermediate water and deep/bottom waters.
(not shown). A cold temperature bias would result in greater CFC-11 concentrations compared to observations. We find that CFC-11 concentrations are lower than observations and therefore suspect that temperature is not a large factor in these differences. The mixed layer depths in CCSM4 are underestimated compared to observations [Danabasoglu et al., 2011]. Mixed layer depths particularly in the southeast Pacific, a major formation region for SAMW and AAIW, are underestimated by up to approximately 200 m. Shallower mixed layers may result in inaccurate formation of SAMW and potentially less CFCs accumulating within SAMW. These shallow mixed layers may help explain why lower thermocline and intermediate waters are under ventilated within the model. Lastly, the westerly wind stress within the Southern Hemisphere is increased within CCSM4 relative to observations. Stronger wind stress may result in the surface concentrations of CFC-11 being overestimated. The CFC-11 inventory within the upper 500 m (Figure 3.6), suggests that the model does overestimate CFC-11 concentrations.
Chapter 4

Comparison of Subantarctic Mode Water and Antarctic Intermediate Water in the South Pacific Between NCAR-CCSM4 and Observations

4.1 Background

Average formation rates for Subantarctic Mode (SAMW) and Antarctic Intermediate Water (AAIW) in the South Pacific are calculated from the National Center for Atmospheric Research Community Climate System Model version 4 (NCAR-CCSM4), using chlorofluorocarbon (CFC-12) inventories. These inventories are compared to those calculated earlier from observations. CCSM4 accurately simulates the southeast Pacific as the region of formation for SAMW and AAIW. Model formation rates for SAMW are 3.4 Sv, about one-third of the observational rate. Shallow mixed layers and insufficient meridional transport of CFC waters in CCSM4 are likely reasons for lower SAMW formation rates. For AAIW in CCSM4, a formation rate of 8.1 Sv is higher than observations. Higher CFC-12 inventories in CCSM4, particularly in the southwest Pacific, and higher surface inventories are likely reasons for greater formation rates of AAIW. This comparison is useful for understanding the uptake and transport of other gases by the model.

4.2 Introductory remarks

Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW) are large volume, lower thermocline and intermediate water masses that fill the Southern Hemisphere subtropical gyres. They ventilate the subtropical gyres with atmospheric gases, and transfer climatically and biologically important properties such as heat,
freshwater, nutrients, and oxygen into the interior ocean [Toggweiler et al., 1991; Talley, 2003; Sallee et al., 2006; Talley, 2008]. SAMW and AAIW are also responsible for a significant fraction of the uptake of anthropogenic CO$_2$ in the world’s oceans [Sabine et al., 2004; Mikaloff-Fletcher et al., 2006]. Thus, variations in SAMW and AAIW formation may have an important role in climate change.

The focus of this study is to compare the formation rates of SAMW and AAIW from the National Center for Atmospheric Research Community Climate System Model version 4 (NCAR-CCSM4) to formation rates from observations by Hartin et al., [2011] using chlorofluorocarbon inventories. The purpose is to assess how well the model simulates the formation of SAMW and AAIW in the South Pacific. Chlorofluorocarbons (CFC-11 and CFC-12) are conservative oceanic tracers that are used to evaluate circulation, water mass ages, and formation rates [e.g., Fine, 2011]. Importantly, CFCs provide a direct analogue to the physical processes of uptake and storage of carbon in the global ocean. These data allow for the direct comparison of model CFC output with observations.

In a recent evaluation of CCSM4, Weijer et al. [2012] find that in all three sectors of the Southern Ocean to 30°S, model CFC-11 and CFC-12 concentrations in lower thermocline and intermediate waters are less than observations. This study sets out to quantify how the model deficiency is linked with biases in the inventories and formation rates of SAMW and AAIW in the South Pacific. However, we will suggest that AAIW model inventories are actually higher due to a combination of high surface concentrations and a lack of observations within the southwest Pacific.
4.3 Data

4.3.1 Hydrographic observations

The observational data used in this study are the same data used in Hartin et al. [2011]. The data are from World Ocean Circulation Experiment (WOCE) sections collected in the 1990s, Climate Variability and Predictability (CLIVAR) collected in the 2000s, and data collected on board the R/V Knorr in austral winter 2005 in the southeast Pacific (http://www-pord.ucsd.edu/~ltalley/aaiw/).

4.3.2 Model description

The National Center for Atmospheric Research (NCAR) Community Climate System model version 4 (CCSM4) is a global coupled ocean, atmosphere, sea-ice, land surface general circulation climate model. The atmospheric model is the NCAR Community Atmospheric Model version 4 with 26 levels in the vertical, and an approximate grid spacing of 1.25° x 0.9°. The ocean model is the NCAR implementation of the Parallel Ocean Program version 2 with 320 x 384 points, and 60 vertical levels, with an approximate grid spacing of 1.11° x 0.54° and finer resolution in the tropics [Gent et al., 2011]. CCSM4 made improvements compared to CCSM3. For example, there is a significant reduction in the excessive uptake of CFCs within the Southern Ocean [Danabasoglu et al., 2011]. For more information on CCSM4, see Gent et al. [2011]. Surface fluxes of CFC are calculated from 1931.5 through 2008.5, following OCMIP 2 protocols [OCMIP, 2000]. Instead of directly using the atmospheric concentrations in OCMIP, atmospheric winds, atmospheric pressure and sea-ice fraction are used in computing the fluxes of CFCs to the surface ocean [Smith et al., 2010].
4.3.3 Defining SAMW and AAIW

The coldest, freshest, and densest variety of SAMW is formed in the southeast Pacific, just west of the Drake Passage [McCartney, 1977; 1982]. It is the main region supplying both SAMW and AAIW to the Pacific. SAMW is found north of the Subantarctic Front (SAF), forming in deep winter mixed layers, usually >500 m [Holte et al., 2012]. SAMW is characterized by a minimum in potential vorticity and high oxygen and CFC concentrations, occupying the lower thermocline of Southern Hemisphere oceans [Fine et al., 2001]. Within the model, we define SAMW as the density layer in the 26.8 - 27.0 kg m$^{-3}$ range, based on the density of the deepest winter mixed layer in the southeast (Figure 4.1), and a minimum in potential vorticity (not shown). However, the mixed layer depth in the model is not as deep, and potential vorticity is not as low as in observations [Weijer et al., 2012]. AAIW forms equatorward of the Polar Front (PF) and subducts at the SAF, characterized by a salinity minimum [e.g. Hanawa and Talley, 2001; Sloyan and Rintoul, 2001b]. In CCSM4, AAIW is defined in the 27.0 - 27.4 kg m$^{-3}$

Figure 4.1: Average CCSM4 winter mixed layer depths (m) from 2000 to 2005, with potential density (kg m$^{-3}$) contours in black.
density range, based on the location of the salinity minimum, and is poleward of the deepest mixed layer. These model density surfaces also correspond to similar density surfaces used to identify SAMW and AAIW in Hartin et al., [2011].

4.4 Methodology

4.4.1 CFC-12 inventory calculation

CFC-12 was chosen as the compound to use because it continued to increase in the atmosphere for a longer time as compared with CFC-11. CFC-12 inventories are calculated for SAMW and AAIW using a technique described in earlier work [Orsi et al., 1999; Smethie and Fine, 2001; Rhein et al., 2002; Willey et al., 2004; LeBel et al., 2008]. As in Hartin et al. [2011]:

\[
\text{CFC}_{\text{inv}} = \rho \sum ([\text{CFC}]_{(ij)} \cdot A_{(ij)} \cdot D_{(ij)})
\]

(4.1)

where \( \text{CFC}_{\text{inv}} \) is the CFC-12 inventory (moles), \( \rho \) is the density of water (kg m\(^{-3}\)), \([\text{CFC}]_{(ij)}\) is the CFC-12 concentration (pmol kg\(^{-1}\)) at latitude (i) and longitude (j), \( A_{(ij)} \) (m\(^2\)) is the area of the corresponding grid box, and \( D_{(ij)} \) (m) is the thickness of each water mass. CFC inventories in the model are calculated from the five member ensemble averaged over 2005. The inventories for SAMW (26.8 - 27.0 kg m\(^{-3}\)) are calculated between the SAF and the equator and for AAIW (27.0 - 27.4 kg m\(^{-3}\)) from the PF to 20°N. The boundaries for both SAMW and AAIW extend from 150°E to 70°W. SAF and PF locations from the model are fairly realistic as compared to the observational data [Weijer et al., 2012]. Therefore, for ease of comparison, we choose to use the observational frontal locations from Orsi et al. [1995] as our southern boundaries for the inventory calculations.
4.4.2 Water mass formation rate calculation

Average water mass formation rates over the period of CFC-12 input are calculated based on methods from [Smethie and Fine, 2001; Kieke et al., 2006; LeBel et al., 2008; Hartin et al., 2011]:

\[
R = \frac{\text{CFC}_{\text{inv}}}{\rho \int_{t_0}^{t_1} [C_s(t) \cdot \text{sat}] dt}
\]  

(4.2)

where \(C_s(t)\) (pmol kg\(^{-1}\)) is the CFC-12 concentration at the source at equilibrium with the atmosphere for the years 1970 to 2005, and \(\text{sat}\) is the CFC-12 percent saturation at the source. When using this equation, the percent saturation at the time of formation and the formation rate are both assumed to be constant over the period of CFC-12 input. See section 2.6.3 for a discussion of the error involved in assuming a constant formation rate. Therefore, CFC-based water mass formation rates are the average for SAMW and AAIW within the South Pacific over the major period of CFC-12 input from 1970 to 2005.

Percent saturations relative to the 2005 atmosphere are calculated after Warner and Weiss [1985] by comparing the model CFC-12 oceanic concentrations to the atmospheric concentrations from 2005. Model CFC-12 saturations within the mixed layer of SAMW in the southeast Pacific are 94% saturated with respect to the 2005 atmosphere, which compares well with the observed value of 95%. Poleward of the SAF in the model mixed layer at the 27.2 kg m\(^{-3}\) isopycnal, AAIW is 82% saturated relative to the 2005 atmosphere, which is lower than observations of 85%. However, once AAIW subducts below the SAF, average model saturations decrease to 54%, below the observed value of 60%. The lower model saturations suggest less CFC-12 penetrating into the interior along AAIW isopycnals (see section 4). It is this saturation of 54% that is used in the formation rate calculation.
4.5 Discussion

Inventory maps allow a spatial analysis of the regions of CFC uptake and formation for SAMW and AAIW. The CCSM4 model CFC-12 inventories for both SAMW and AAIW simulate the maxima in the southeast Pacific as shown in the observations (Figures 4.2 and 4.3). In both the simulated SAMW and AAIW there is a CFC-12 inventory (>0.7 moles km\(^{-2}\)) maximum centered at 90°W, and another relative maximum (>0.5 moles km\(^{-2}\)) centered at about 180°. A secondary maximum is also present in the observations for SAMW and AAIW, although with lower inventories and centered at 150°W for SAMW and closer to 170°W for AAIW. The model AAIW maxima are found equatorward of the PF, and poleward of the SAMW maximum. The CCSM4 inventory maps agree well with other studies that suggest the southeast Pacific as a major site of formation for SAMW and AAIW [McCartney, 1982; Sloyan and Rintoul, 2001b; Iudicone et al., 2007; Hartin et al., 2011].

The model SAMW and AAIW CFC-12 inventory maxima are not continuous across the South Pacific. The western and eastern Pacific maxima are separated by an inventory minimum between 120°W and 130°W, potentially due to enhanced mixing related to the East Pacific Rise. The majority of the model CFC-12 inventory lies within the subtropical gyre and concentrations reach nearly zero levels as SAMW and AAIW approach 30°S. There is a significant decrease in the CFC-12 inventory equatorward of 50°S and 60°S for SAMW and AAIW, respectively. In other words, the simulated
Figure 4.2: CFC-12 inventories (moles km\(^{-2}\)) within SAMW in 2005 a) a combination of WOCE, CLIVAR, and data collected in 2005 all corrected to a common collection date of 2005 (26.8 – 27.06 kg m\(^{-3}\)) , black dots show sample locations, b) SAMW in 2005 (26.8-27.0 kg m\(^{-3}\)) from CCSM4 output.
**Figure 4.33:** CFC-12 inventory (moles km$^{-2}$) within AAIW for 2005 a) a combination of WOCE, CLIVAR, and data collected in 2005 all corrected to a common collection date of 2005 (27.06-27.4 kg m$^{-3}$), black dots show sample locations b) AAIW (27.0-27.4 kg m$^{-3}$) in 2005 from CCSM4 output.
SAMW and AAIW do not carry CFCs as far equatorward as observed. For example, the 0.5 mol km$^{-2}$ contour in observations extends to approximately 35$^\circ$S, while the 0.5 mol km$^{-2}$ contour in the model inventories only extends to approximately 45-50$^\circ$S. This weak CFC equatorward spreading is likely explained by biases in the parameterized meridional transport by mesoscale eddies, which are widely believed to be the main vehicle of the meridional tracer transport in the Southern Ocean [i.e., Karsten et al., 2002; Lachkar et al., 2007].

<table>
<thead>
<tr>
<th></th>
<th>Observations</th>
<th>Model</th>
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</thead>
<tbody>
<tr>
<td><strong>SAMW</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inventories</td>
<td>16x10$^6$ moles</td>
<td>7.5x10$^6$ moles</td>
</tr>
<tr>
<td>Saturations</td>
<td>95 %</td>
<td>94 %</td>
</tr>
<tr>
<td>Formation Rates</td>
<td>7.3 ± 2.1 Sv</td>
<td>3.4 Sv</td>
</tr>
<tr>
<td><strong>AAIW</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inventories</td>
<td>8.7x10$^6$ moles</td>
<td>11.9 x10$^6$ moles</td>
</tr>
<tr>
<td>Saturations (equatorward of SAF)</td>
<td>60 %</td>
<td>54 %</td>
</tr>
<tr>
<td>Saturations (poleward of SAF)</td>
<td>85 %</td>
<td>82 %</td>
</tr>
<tr>
<td>Formation Rates</td>
<td>5.8 ± 1.7Sv</td>
<td>8.1 Sv</td>
</tr>
</tbody>
</table>

Table 4.1: SAMW and AAIW inventories, mixed layer saturations and formation rates for both observations and model. Observations from Hartin et al. (2011).

Total CFC-12 inventories for SAMW from observations are 16x10$^6$ moles, which is significantly higher than the 7.5x10$^6$ moles estimated within CCSM4 (Table 1). These inventories correspond to formation rates of 7.3 ± 2.1 Sv for observations and 3.4 Sv for CCSM4. For this study, we use the observational formation rates of SAMW that are
formed and circulate around the South Pacific, and do not include SAMW that has been transported out of the subtropical gyre [Hartin et al., 2011]. The underestimation in the inventory and formation rate within the model may be attributed to shallower than observed mixed layers and insufficient meridional transport of CFC waters equatorward. In order to verify the first assumption, the inventories (mol km$^{-2}$) are divided by the mixed layer depth (m) to obtain a CFC-12 concentration in the mixed layer in mol km$^{-3}$ (Figure 4.4). For the observations across the entire South Pacific, we used the Commonwealth Scientific and Industrial Research Organization (CSIRO) Atlas of Regional Seas 2009 (CARS2009) [Ridgway et al., 2002] monthly mixed layer depth climatology, and the monthly mean output of mixed layer depth from CCSM4. When comparing the observations and model output for SAMW in Figure 4.1, it is apparent that the CFC-12 concentration in the mixed layer along the SAF and within the mixed layer are similar between the model and observations, which suggests that a low bias in the simulated CFC inventories are in part explained by a shallow bias in the model mixed layer. The shallow mixed layer tends to concentrate the CFCs, shown by the high CFC-12 concentration in the mixed layer from Figure 4.4. The model-simulated winter mixed layer depths in these regions are indeed only approximately 150m, which is significantly shallower than the average winter mixed layer depth of >250m from CARS2009 climatology [Weijer et al., 2012]; see also Sloyan and Kamenkovich [2007] for a similar conclusion for many AR4 climate models.

A possible reason for the shallow bias within the CCSM4 mixed layer may be due to the parameterization of the mixing processes involved in mixed layer formation. The submesoscale parameterizations used in the model tend to make the mixed layer
shallower than observations, with the greatest effects in the high latitudes [Fox-Kemper et al., 2011].

Equatorward of the deep mixed layer, CFC concentrations and inventory estimates drop off dramatically and are low compared with observations. Insufficient meridional transport within the model is evident in the inventories, with much larger values in the subtropical gyre in the observations. In addition, too weak vertical mixing is noticeable in CCSM4 as higher potential vorticity at the base of the mixed layer,

Figure 4.4: CFC-12 per unit volume (moles km\(^{-3}\)) for SAMW for a) observations; and b) CCSM4. The dashed line is the SAF and the solid line the PF, taken from Orsi et al. (1995).

compared with observations [Weijer et al., 2012]. This combination of weaker mixing within the mixed layers, and insufficient meridional transport of high CFC waters can result in an underestimation of the SAMW inventories. For example, if less CFCs are
removed from the mixed layer, surface concentrations will tend to be too high and that in
turn will limit the uptake of more CFCs from the atmosphere. These lower SAMW
inventories and formation rates in the model also imply weaker ventilation of the
subtropical gyre with atmospheric gases in general.

Total CFC-12 inventories for AAIW in current observations are $8.7 \times 10^6$ moles

and $11.9 \times 10^6$ moles in CCSM4. These inventories correspond to formation rates of $5.8$
$\pm 1.7$ Sv for observations, which was interpreted by Hartin et al. (2011) as a lower
boundary on the formation rates of AAIW, and $8.1$ Sv for CCSM4. A closer inspection
of the observational and model estimates offers an explanation for the differences.

Surface concentrations and surface inventories reported in Weijer et al. [2012] in the

Figure 4.5: CFC-12 per unit volume (moles km$^{-3}$) for AAIW for a) observations
and b) CCSM4. The dashed line is the SAF and the solid line the PF, taken from
Orsi et al. (1995).
model are higher than observations; particularly within the ACC and along AAIW outcrops. This overestimation in surface concentrations may be due to a combination of a cold bias in CCSM4, poleward of 45°S [Danabasoglu et al., 2011] and weak meridional transport of CFCs. This is also evident in the concentrations in the mixed layer shown in Figure 4.6. The mixed layer depths are shallow poleward of the SAF. Therefore, these calculations offer estimates of surface-like conditions that are influencing the outcropping isopycnals of AAIW. There are higher concentrations between the SAF and PF in the model, not evident in the observations, due to the high surface concentrations contributing to the overestimation of the CFC-12 inventories in AAIW.

The model also has higher AAIW CFC-12 inventories in the central and southwest Pacific, where there is a lack of hydrographic observations, particularly between 150°E and 180°. In order to estimate the potential significance of a lack of data resolution for inventory estimates in the southwest Pacific, we eliminated the model output in the southwest Pacific at all latitudes from 150°E to 180°. This resulted in a substantially reduced inventory of 9.9 x 10^6 moles and a formation rate of 6.7 Sv, as compared with from 11.9 x 10^6 moles and 8.1 Sv in the calculation with full data. Since this is also a region of significant gaps in data coverage, it remains unclear whether the difference between the observed and simulated inventories corresponds to model biases in this region, such as shallow mixed layer depths or a lack of data coverage in the observations.
4.6 Conclusions

Comparisons of CFC-12 inventories and formation rates of SAMW and AAIW from observations and model output are important for validating a model. CCSM4 accurately depicts the southeast Pacific as the main region of formation for SAMW and AAIW. Inventories and formation rates of SAMW in the South Pacific in CCSM4 are significantly less than observations, mainly due to the shallow bias in the model mixed layer depths and insufficient meridional transport of high CFC waters into the interior. The inventories and formation rates for AAIW in CCSM4, by contrast, are higher than the observational estimates, primarily due to higher model inventories in the southwest Pacific and higher surface concentrations. Causes for the latter biases are not clear, but may be related to a combination of a cold bias in sea surface temperatures poleward of 45°S in CCSM4 [Danabasoglu et al., 2011] and weak meridional transport of CFC waters.

Differences in the modeled and observed CFC-12 concentrations, saturations, and inventories emphasize the need for further model improvement in ocean-atmosphere exchange and upper ocean parameterizations. They also highlight the need for more hydrographic observations within the southwest Pacific. In the model, reduced meridional penetration of CFCs from the source regions further suggests that CO₂ uptake and sequestration also may be underestimated by model simulations.
Chapter 5

Formation of Mode and Intermediate Waters in the South Pacific during the Last Glacial Maximum: A Model Study using NCAR-CCSM3

5.1 Background

In the modern ocean, Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW) are large-volume intermediate water masses that transport climatically important properties such as heat, freshwater, and CO$_2$ equatorward into the Southern Hemisphere subtropical gyres. Some of the freshest and coldest SAMW and AAIW formed in today’s oceans are found in the southeast Pacific. The objective of this study is to quantify and compare changes in the formation rates of Glacial Subantarctic Mode Water (G-SAMW) and Glacial Antarctic Intermediate Water (G-AAIW) during the Last Glacial Maximum (LGM; 21,000 years ago) with SAMW and AAIW during the preindustrial (PI) to see if the differences provide insights to future changes. The water masses are simulated for the South Pacific in the National Center for Atmospheric Research (NCAR) Community Climate System Model version 3 (CCSM3).

Water mass formation rates are computed and compared from two methods, thermodynamic (surface fluxes) and dynamic methods. The thermodynamic method does not account for contributions from mixing, while the dynamic method measures the total rate at which water enters the permanent thermocline. Formation rates of both G-SAMW and G-AAIW calculated using surface fluxes suggest destruction of these water masses at the surface. While, using the dynamic method, G-SAMW and G-AAIW over the South Pacific exhibit increased subduction rates, from 4.3 Sv in the PI to 8.9 Sv in the LGM simulation for SAMW, and 4.3 Sv in the PI to 8.3 Sv in the LGM simulation for AAIW.
We interpret these results from the dynamic method to represent the total amount of water forming in the South Pacific. Competing processes of upper ocean stratification due to enhanced sea-ice cover and enhanced wind stress over the Southern Hemisphere in the LGM simulation are responsible for the modeled changes in G-SAMW and G-AAIW. Future projections suggest both an increase in upper ocean stratification and an increase in wind stress under global warming scenarios. This study emphasizes the importance of properly simulating sea-ice cover and westerly wind circulation as key processes for correctly diagnosing changes in SAMW and AAIW – and therefore, also ocean heat transport, nutrient distributions, and CO$_2$, under past and future climate conditions.

5.2 Introductory remarks

Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW) are large-volume, relatively cool water masses that sequester significant quantities of atmospheric gases, such as CO$_2$ and O$_2$, at formation [e.g., Sabine et al., 2004; Mikaloff-Fletcher et al., 2006]. Half of the northward transport of anthropogenic CO$_2$ in the subsurface is contained within SAMW and AAIW [Ito et al., 2010]. Along with the uptake of CO$_2$, SAMW and AAIW also play a significant role in the transfer of other climatically important properties, such as heat and freshwater, to the interior of the Southern Hemisphere subtropical gyres, in addition to ventilating the subtropical gyres [e.g., Gordon, 1986; Fine et al., 2001; Sabine et al., 2002]. These water masses supply a significant portion of nutrients to the upper ocean in equatorial regions, fueling primary production [Toggweiler et al., 1991; Sarmiento et al., 2004].
SAMW and AAIW are important components of the overall global meridional overturning circulation. North Atlantic Deep Water exported to the Southern Ocean is in part balanced by the formation and northward transport of SAMW and AAIW [Gordon, 1986; Sloyan and Rintoul, 2001a]. AAIW is characterized by low temperatures, a vertical salinity minimum and high oxygen concentrations. Its formation is linked to the Circumpolar Deep Water, which upwells around Antarctica and is carried northward via Ekman transport as Antarctic Surface Water (AASW). AASW is subsequently converted to AAIW through air-sea fluxes equatorward of the Polar Front (PF) and subducts at the Subantarctic Front [SAF; e.g., Sloyan and Rintoul, 2001b].

Sea-ice cover plays a major role in the transfer of heat and freshwater into the ocean. Present day AAIW formation has been shown to be particularly sensitive to the sea-ice extent and the equatorward transport of sea-ice [Saenko and Weaver, 2001]. The salinity minimum associated with present day and PI AAIW exists in part due to the input of fresh water from melting sea-ice [Saenko and Weaver, 2001; Duffy et al., 2001].

SAMW is formed from the deepening of mixed layers during wintertime convection [Holte et al., 2012] and subsequent mixing [Sloyan et al., 2010]. SAMW is formed north of the SAF throughout the Southern Hemisphere, with the main site of formation in the southeast Pacific [McCartney, 1977; Hartin et al., 2011]. It occupies the lower pycnocline of the Southern Hemisphere subtropical gyres and is characterized by a vertically homogenous layer of low potential vorticity.

SAMW and AAIW are transported eastward with the Antarctic Circumpolar Current (ACC), and then transported northward into the southern Indian, Pacific, and Atlantic subtropical gyres [e.g. Talley, 2003; Speich et al., 2007]. Therefore, due to their
large volumes, high dissolved gas concentrations and a connection to each ocean basin, SAMW and AAIW can play an important role in the climate system.

5.3 Last Glacial Maximum

The climate of the Last Glacial Maximum (LGM; ~ 21,000 years ago) was characterized by globally cooler temperatures and increased ice sheet cover [Adkins et al., 2002; Peltier, 2004]. Atmospheric pCO$_2$ was at 180-200 ppm, or 80-100 ppm lower than preindustrial values [Petit et al., 1999; Monnin et al., 2001]. During the LGM there was a fundamental reorganization of the global ocean circulation, a shutdown of North Atlantic Deep Water (NADW) replaced with an intermediate water mass. There were also major shifts in the transfer of CO$_2$ between the oceans and atmosphere. Past changes in global atmospheric CO$_2$ concentrations over glacial and interglacial cycles are believed to be driven by two processes; physical, e.g. ventilation and stratification changes of intermediate to deep waters, and biological, e.g. changes in nutrient distributions and biological productivity [Siegenthaler and Wenk, 1984; Francois and Altabet, 1997; Sigman and Boyle, 2000; Toggweiler et al., 2006].

Detailed paleo-proxy studies of SAMW and AAIW in the LGM are limited, especially within the South Pacific. Sediment cores from the LGM within the eastern South Pacific and equatorial Pacific suggest increased ventilation and increased production of AAIW. Muratli et al.[2010], using rhenium and manganese concentrations in sediments along the Chilean margin, concluded that AAIW production and oxygen concentrations both increased in the LGM. Nameroft et al. [2004] attributed changes in redox sensitive trace metals along the Mexican continental margin oxygen minimum
zone to changes in regional export production and or changes in ocean circulation, with these changes traced back to SAMW. Using a combination of nutrient proxies and $\delta^{13}C$ and $\delta^{18}O$, Matsumoto et al. [2002] interpreted increased formation rates of SAMW and AAIW in the Pacific. In the western Pacific, Bostock et al. [2004] used benthic foraminiferal $\delta^{13}C$ to show that AAIW was a thicker, more dominant water mass in the LGM with increased influence on the equatorial regions. This also agrees with a study by Lynch-Steiglitz et al. [1994] who concluded that transport of salty Indian waters along the ACC was reduced to the western Pacific in the LGM and replaced by more poleward sourced surface waters and AAIW production there. AAIW formation and circulation may prove to be regionally variable during the LGM. Evidence in the Indian and southwest Pacific suggest that enhanced AAIW formation was during the deglacial rather than during the LGM [Pahnke and Zahn, 2005; Jung et al., 2009]. In the South Atlantic studies suggest that AAIW was a consistent presence during the LGM, however, it may be less ventilated than today due to increased sea-ice expansion or decreased wind stress during the LGM [Makou et al., 2010; Hendry et al., 2012]. A similar study to ours by Wainer et al. [2012], looked at formation rates of intermediate water in the NCAR-CCSM3 model and found that increased Ekman transport drove increased production of intermediate water during the LGM.

Proxy studies using $\delta^{15}N$ have identified reduced zones of denitrification in both the North and South Pacific during the LGM due to a combination of lower glacial temperatures, increasing $O_2$ solubility, and enhanced ventilation of thermocline waters [Kienast et al., 2002; Galbraith et al., 2004; Nameroff et al., 2004]. Support for this comes from a modeling study by Meissner et al. [2005] who found enhanced production
and transport of O$_2$ rich thermocline to intermediate waters into the eastern tropical Pacific, thereby reducing the denitrification zones during the LGM. However, there is some debate that the lower denitrification rates in the equatorial Pacific in the LGM were due to decreased input of nitrate from the Southern Ocean, rather than changes in water mass ventilation [Robinson et al., 2007; Robinson et al., 2009].

Though limited in number and distribution, available paleo-proxy studies point to significant increases in the circulation and ventilation of SAMW and AAIW in the LGM. Here, we assess the physical mechanisms - surface fluxes and subduction - responsible for the apparent changes in SAMW and AAIW in the LGM, using the National Center for Atmospheric Research (NCAR) Community Climate System Model version 3 (CCSM3). The implications of this study are not limited to the LGM. Both because of the availability of proxy data and the large differences with the PI climate, the LGM represents a convenient case study for analyzing sensitivity of SAMW/AAIW water masses to climate change. This analysis is timely because of the inconclusiveness about modern and future changes in intermediate water formation, and its potential role in CO$_2$ sequestration and transport of O$_2$ and nutrients to the equatorial regions.

5.4 Model description

The NCAR-CCSM3 is a global coupled ocean, atmosphere, sea-ice, land surface general circulation climate model. A detailed description of the model is found in Collins et al. [2006]. The atmospheric model is the NCAR Community Atmospheric Model version 3 with 26 levels in the vertical, and an approximate grid spacing of 2.8°. The ocean model is the NCAR implementation of the Parallel Ocean Program with 320x384
points and 40 levels extending down to 5.5 km, with an approximate grid spacing of 1° and greater resolution in the tropics and the North Atlantic. The sea-ice model uses the same horizontal grid as the ocean component. The preindustrial (PI) simulation is forced with the appropriate conditions prior to industrialization, A.D. 1800, following the protocols of the Paleoclimate Modelling Intercomparison Project Phase 2 [Otto-Bliesner et al., 2006]. The Last Glacial Maximum (LGM) simulation is forced with changes in atmospheric concentrations of carbon dioxide, methane and nitrous oxide, a 2-3 km thick ice sheet, and global sea level reduced by 120m. The LGM ocean is initialized by using the anomalies of potential temperature and salinity from the LGM simulation from the Climate System Model version 1.4, which is then applied to the CCSM3 PI simulation. The mean climate results presented in this study are monthly averages over the last 50 years of the LGM and PI simulations.

**5.5 Identification of SAMW and AAIW**

In order to understand changes in SAMW and AAIW, we identify SAMW and AAIW in the LGM using similar characteristics found in both the present and PI. First, we compare SAMW and AAIW in the PI to present day observations (Figures 5.1 & 5.2). In CCSM3 in the PI, SAMW is defined as the 26.9-27.2 kg m\(^{-3}\) isopycnal layer in the South Pacific. It also has a relative low in potential vorticity (a measure of the stratification of the water mass), although not as low as modern observations (Figures 5.1a, b). AAIW is defined as the 27.2-27.5 kg m\(^{-3}\) layer, and similar to observations is characterized by a salinity minimum extending north of the equator (Figures 5.2 a, b).
Both SAMW and AAIW are denser, colder, and saltier in the LGM, in comparison to the PI. To distinguish between the traditional definitions of SAMW and AAIW in the modern ocean, we will use G-SAMW and G-AAIW to identify these water masses during

**Figure 5.1:** Potential vorticity (10^{-10} \text{ m}^{-1} \text{ s}^{-1}) along 88^\circ \text{W} for a) hydrographic observations, b) preindustrial simulation and c) LGM simulation.
the LGM. In the LGM simulation, G-SAMW is identified based on a slight minimum in potential vorticity at the surface and the relationship with deep mixed layers in the

southeast Pacific, defined from 27.6 to 28.2 kg m\(^{-3}\) (Figure 5.1 c). Critical to SAMW formation in the modern South Pacific is convection within deep (> 500 m) mixed layers [Holte et al., 2012]. The magnitude of the mixed layer depth in the LGM simulation is

**Figure 5.2:** Salinity along 88°W for a) hydrographic observations, b) preindustrial simulation and c) LGM simulation (note change in scale).
comparable to the PI simulation, approximately 150-200 m (Figure 5.3). However, the location of the deepest mixed layers shift equatorward compared to the PI by more than 5 degrees. In the LGM, G-SAMW is characterized by a layer of low potential vorticity particularly at surface. This low is not as strong as in the PI, suggesting less intense convection and shallower mixed layers. G-SAMW is on average saltier by 1.0 psu (Figure 5.2c) and colder by 3-4 °C (not shown) in the LGM, in comparison to the PI.
These model temperatures agree well with temperature proxies in the LGM of a 4-5° cooler thermocline [Lynch-Stieglitz et al., 1994; Matsumoto et al., 2002].

In the LGM, G-AAIW is defined from 28.2 - 29.0 kg m\(^{-3}\) and is no longer characterized by a salinity minimum; instead salinity gradually increases with depth (Figure 5.2c). G-AAIW is identified based on its location poleward of G-SAMW formation and its presence at intermediate depths. The lens of fresh surface water that contributes to the low salinity signal of AAIW in the PI is not present in the LGM over the isopycnals of AAIW. In the LGM, G-AAIW is on average saltier by 1.5-2.0 and colder by 2-3°C than AAIW in the PI. Southern Ocean paleo-salinities in the LGM are saltier by approximately 2.4 compared to modern day values [Adkins et al., 2002].

The deepest mixed layers and outcropping surfaces of G-SAMW and G-AAIW shifted equatorward by 5 - 7° latitude in the LGM, agreeing with previous studies suggesting that the PF shifted northward by up to 7° [Kumar et al., 1995; Gersonde et al., 2005]. Therefore, G-SAMW and G-AAIW form further equatorward in the LGM simulation, consistent with studies which suggest that the ocean circulation and subtropical gyres were compressed in the LGM [Otto-Bliesner et al., 2006].

### 5.6 Surface fluxes (air-sea and ice-sea)

Surface fluxes of heat and freshwater play a critical role in the transformation of water masses by modifying the density of the surface waters. Surface fluxes drive overturning and decrease or increase the surface stratification. In order for a water parcel to subduct below the mixed layer, the surface waters need to re-stratify over the seasonal cycle [Nurser and Marshall, 1991; Marshall and Marshall, 1995]. Stratification of the
surface waters is particularly strong during the austral summer months from sea-ice melt in the LGM simulation. This is achieved through changes in fluxes of heat and freshwater. The buoyancy flux from the atmosphere/ice to the ocean $B$ is computed following Karstensen and Lorbacher [2011]:

$$B = -g \rho_s (\alpha F_T + \beta F_S)$$  \hspace{1cm} (5.1)

where $F_T = \frac{-Q_{\text{net}}}{\rho_s C_p}$ and $F_S = (F_w) \cdot S/(1-S/1000)$, $\alpha$ is the thermal expansion coefficient, $\beta$ is the haline contraction coefficient, $Q_{\text{net}}$ is the net heat flux into the ocean from both air-sea and ice-sea fluxes (negative when the ocean losses heat), $\rho_s$ is the sea surface density, $C_p$ is the specific heat capacity of seawater, $F_w$ is the freshwater flux, $S$ is the sea surface salinity and $g$ is the acceleration due to gravity. The negative sign in front of $g$ indicates that a water parcel becomes less buoyant when it gains density. Therefore, a negative $B$ will drive convection, while a positive $B$ will result in increased stratification.

The climatological annual-mean net surface buoyancy-fluxes into the ocean are shown in Figure 5.4. On a large scale in the PI, the ocean has positive buoyancy-fluxes (stratifying) within the subtropical gyre and negative fluxes (convection-inducing) poleward of about 55°S. Freshwater fluxes into the ocean are positive between 40°S and 60°S, due to precipitation and sea-ice melt exceeding evaporation, which would act to stratify the water column. Thermal fluxes dominate the total buoyancy flux further equatorward in the South Pacific.

The spatial patterns of the air-sea and ice-sea buoyancy-fluxes are fairly similar between the PI and LGM. However, there are some significant differences in the SAMW and AAIW isopycnals between the PI and LGM. Total buoyancy fluxes of G-SAMW are more negative, while G-AAIW is more positive in the LGM. From figure 5.4 we can see
that G-AAIW is forming in the regime that defined SAMW in the PI, this being the region of maximum freshwater input from the sea-ice edge. Overall thermal fluxes are lower during the LGM due to the equatorward advance of sea-ice, which inhibits air-sea
fluxes of heat. This is evident in the transformation rates as well (see section 6.1). In the LGM. In the PI, the 40% sea-ice concentration in the South Pacific extends equatorward to about 65°S (not shown). Note that the PI sea-ice cover is slightly enhanced relative to the present day [Otto-Bliesner et al., 2006]. In contrast, sea-ice extent increases dramatically in the LGM (Figure 5.5), with the 40% sea-ice concentration (not shown) extending equatorward to about 55°S. The model sea-ice extent agrees well with the range of paleo-proxy evidence for the LGM of 65-55°S [Crosta and Pichon, 1998; Wolff et al., 2003; Gersonde et al., 2005]. As in the PI, the winter-time sea-ice in the LGM extends over the outcropping isopycnals of AAIW.

5.7 Water mass formation

Water mass formation rates can be computed using the thermodynamic and dynamic methods [Marshall et al., 1999]. The surface flux thermodynamic method is based on the relationship between the surface buoyancy fluxes and water mass formation. In particular, Walin [1982] showed that the diapycnal volume flux across an outcropping isopycnal surface is essentially equal to the transformation of surface waters from one density to another. The dynamic method measures the rate at which water crosses from the mixed layer into the permanent thermocline.

5.7.1 Thermodynamic method

Water mass transformation rates are calculated after Speer and Tziperman [1992], Speer et al. [1995], Downes et al. [2011] and Brambilla et al. [2008];

\[ F(\sigma_\theta) = -\frac{1}{\Delta \sigma} \int_A \left( \frac{\alpha_{Q_{net}}}{c_p} \right) dA + \frac{1}{\Delta \sigma} \int_A \rho_s \left( \frac{\beta S(FW)}{1-S} \right) dA \quad (5.2) \]
Figure 5.5: a) summer sea-ice concentration during the PI, b) summer sea-ice concentration during the LGM, c) winter sea-ice concentration during the PI, d) winter sea-ice concentration during the LGM and e) fractional winter sea-ice concentration between the LGM and PI simulations, with outcropping isopycnals of SAMW and AAIW in black contour. Note the increase in sea-ice over AAIW isopycnals.
where $F(\sigma_0)$ is the water mass transformation due to surface (air-sea and ice-sea) fluxes, integrated between $\sigma_0$ and $\sigma_0 + \Delta \sigma$ density surfaces and from $150^\circ$E to $70^\circ$W. Once the transformation rate is calculated, the annual mean formation rate $M$ (in Sv) between isopycnals $\sigma_{01}$ and $\sigma_{02}$ is estimated by:

$$M = -[F(\sigma_{02}) - F(\sigma_{01})]$$  \hspace{1cm} (5.3)

where, $\sigma_{01} < \sigma_{02}$. Positive values of $M$ correspond to subduction (water mass formation) in the density range, while negative values of $M$ correspond to transformation to a less dense density surface. Another way to interpret equation 3 is, if the volume of water leaving the $\sigma_{01}$ isopycnal is larger than the volume leaving the $\sigma_{02}$ isopycnal then there is

**Figure 5.6**: Schematics to describe the processes of transformation and formation (positive and negative). (a) Schematic of transformation of surface water masses from one density to the next. (b) Positive water mass formation (subduction) from the surface mixed layer into the ocean interior driven by the convergence of surface water. (c) Negative water mass formation (obduction) from the ocean interior to the surface mixed layer driven by the divergence of surface water. Modified from Brambilla et al. [2008].
a convergence of water that leads to subduction or formation of a water mass with a
density of $\sigma_{\theta}$ (Figure 5.6). The other sources of mass to the density range are mixing
($M_M$) and boundary sources ($M_B$), if the domain is not completely closed by land [Speer
and Tziperman, 1992]. If we take all sources into account the total water mass balance
over a given density range would equal $M + M_M + M_B = 0$. These potential sources of
heat and freshwater to the domain via the open boundaries of the Southern Ocean are
ignored, and we are calculating surface fluxes alone. This lateral exchange may prove to
be important (see section 5.7.3). Total transformation ($F$) in the PI for SAMW is
characterized by decreasing transport across the entire density range $26.9 - 27.2 \sigma_0$
(Figure 5.7). The thermal component dominates the total transformation leading to a
positive transformation across the SAMW density range, while the freshwater component
contributes to a negative transformation (Table 5.1a). The total transformation for AAIW
is small across the entire AAIW density range, with a significant compensation between
thermal and freshwater components. SAMW formation rates ($M$) in the PI are $10.7 \text{ Sv}$
and $-1.6 \text{ Sv}$ for AAIW (Figure 5.7 c and d). The negative formation rate or obduction for
AAIW represents a transformation of water converted to a lower density range.

The total transformation of G-SAMW in the LGM is characterized by negative
transports across the entire density range dominated by freshwater while the thermal
component contributes to a slight positive transformation. This is the opposite of SAMW
during the PI which was dominated by heat fluxes. As for G-AAIW in the LGM, the
total transformation is negative, with freshwater fluxes dominating this negative
transformation. This negative freshwater flux over G-SAMW and G-AAIW in the LGM
is due to the significant seasonal variability of sea-ice formation and melting,
Contributing to a significant freshwater flux over the density range of G-SAMW. On the other hand, transformation due to freshwater fluxes over G-AAIW is much smaller than those over G-SAMW and less negative compared to AAIW during the PI. This is most likely due to the presence of sea-ice extending further equatorward over G-AAIW over much of the year. In addition, it is the likely cause for the lack of an AAIW salinity minimum in the LGM. Formation rates (M) for G-SAMW in the LGM are -29.7 Sv and -2.4 Sv for G-AAIW. These negative formation in the LGM rates represent transformation of water to a lesser density range.

#### Table 5.1

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<thead>
<tr>
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<th>Preindustrial Thermodynamic Method</th>
<th>Last Glacial Maximum Thermodynamic Method</th>
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<tr>
<td></td>
<td>Heat (Sv)</td>
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</tr>
<tr>
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<td>G-AAIW</td>
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<th>Dynamic Method (Sv)</th>
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<tr>
<td>SAMW</td>
<td>10.7</td>
<td>4.3 Sv</td>
</tr>
<tr>
<td>AAIW</td>
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<td>4.3 Sv</td>
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<th>Transport across 30°S (Sv)</th>
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<td>30°S</td>
<td>thermocline to 30°S</td>
</tr>
<tr>
<td>SAMW</td>
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<td>4.6 – (4.3) = .03</td>
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<tr>
<td>AAIW</td>
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<td>2.4</td>
<td>2.4 – (4.3) = -1.9</td>
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<tr>
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<th>Transport across 30°S (Sv)</th>
<th>Mixing (Sv) to 30°S</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-SAMW</td>
<td>8.9 – (-29.7) = 38.6</td>
<td>6.1</td>
<td>6.1 – (8.9) = -2.8</td>
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<tr>
<td>G-AAIW</td>
<td>8.3 – (-2.4) = 10.7</td>
<td>3.4</td>
<td>3.4 – (8.3) = -4.9</td>
</tr>
</tbody>
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**Table 5.1**: a) heat, freshwater and total surface transformation, b) comparison of the thermodynamic and dynamic methods and c) the effects of mixing between the surface and permanent thermocline and between the permanent thermocline and 30°S.
Note there may be significant mixing between SAMW and AAIW isopycnals, particularly close to the ACC [e.g., Sloyan et al., 2010]. The potential effects of mixing are not included in the thermodynamic method and are discussed below in section 5.7.3.

**Figure 5.7**: Annual mean formation rate (M; subduction and obduction) in Sv (vertical axis), calculated from the spatial integral of the density flux over the domain. Density bin width of Δσθ = 0.1 kg m⁻³, a) PI and b) LGM. Annual mean transformation in Sv (vertical axis) c) PI and d) LGM. Red is thermal contribution, blue is freshwater contribution and black is total. Positive values indicate subduction.
5.7.2 Dynamic method

The annual subduction rate is defined as fluid irreversibly transferred into the permanent thermocline using the following equation (Marshall et al. 1993):

\[ S_{\text{ann}} = -\bar{u}_{\text{ml}} \cdot \nabla h_{\text{ml}} - \bar{w}_{\text{ml}} \]  

(5.4)

where, \( \bar{u}_{\text{ml}} \) and \( \bar{w}_{\text{ml}} \) are the monthly horizontal and vertical velocity components at the base of the deepest winter mixed layer (\( h_{\text{ml}} \)). The first term on the right-hand side of (5.4) is the convergence of volume fluxes within the mixed layer; it will be referred to as the “lateral subduction” term. The second term, the “vertical subduction” term, represents the vertical velocity at the base of the mixed layer. A negative \( S_{\text{ann}} \) represents subduction from the mixed layer into the permanent thermocline, while a positive \( S_{\text{ann}} \) represents obduction or upwelling, from the thermocline into the mixed layer.

Motion within the upper kilometer or so of the ocean is primarily driven by winds [Qiu and Huang, 1995; Huang and Qiu, 1998; Karstensen and Quadfasel, 2002]. The horizontal and vertical velocities within this layer have an important role in the subduction of these water masses. During the LGM, the zonally averaged austral winter wind stress across the Pacific from 140°E - 70°W was stronger by approximately 24% (Figure 5.8). Within the model, the location of the peak surface wind stress at approximately 51°S does not change between the two periods (see section 5.7). An increase in the westerly wind stress contributes to and strengthens the upper ocean circulation through increased Ekman transport and subsequent formation of AAIW [Ribbe, 2001]. Recent observations show a strong relationship between increased circulation through intermediate depths and increased wind stress [Roemmich et al.,]
2007]. Zonally averaged wind stress curl, and the corresponding Ekman pumping/suction, over the Pacific also increased in the LGM (not shown).

Across the South Pacific there are regions of intense subduction and obduction (Figure 5.9). In the PI, intense subduction is found in the southwest Pacific, while in the LGM, the east and central Pacific have more intense subduction as in observations. Modern observations suggest that the southeast Pacific is the region of greatest formation [Hartin et al., 2011]. Sallee et al. [2010], using a similar subduction equation also finds the southwest Pacific as a region of high subduction, particularly for SAMW. During

![Figure 5.8: Zonally averaged austral winter surface wind stress (N m⁻²) across the Pacific from 140 – 300°, blue line is the LGM simulation and the red line is the PI simulation.](image)

both the periods, these strong subduction sites correspond to regions of enhanced negative lateral subduction, greater mixed layer depth and stronger regional wind stress (not shown). The lateral subduction term dominates the formation of SAMW and AAIW
in both the PI and LGM (Figure 5.9). The vertical transfer of fluid over the outcropping isopycnals of SAMW and AAIW is positive across the South Pacific in both periods, consistent with an overall Ekman upwelling.

The total annual averaged formation rate (in Sv) is calculated from the integral of the local negative subduction over the area of outcropping isopycnals [e.g. Goes et al., 2008],

\[ F = \int_A S_{ann} \, dA \quad (5.5) \]

Average PI formation rates for SAMW are 4.3 Sv, and 4.3 Sv for AAIW (Table 5.1). Average LGM formation rates are nearly double the PI rates, with the G-SAMW formation rate at 8.9 Sv and 8.3 Sv for G-AAIW.

**5.7.3 Comparison of thermodynamic and dynamic methods**

It is difficult to directly compare both the dynamic and thermodynamic methods of calculating formation rates. In particular, previous studies have suggested that there may be large differences between these methods, as well as even having different signs [Marshall et al., 1993; Marshall et al., 1999]. We interpret the dynamic rates as the total formation of these water masses, i.e., the amount of water irreversibly passing through the mixed layer and into the permanent thermocline within the South Pacific.

In contrast, the thermodynamic method estimates the rate at which the water in a particular density class is formed through buoyancy exchanges between the ocean and atmosphere and ice. In this study, we treat the rates calculated from the surface flux calculation as the total amount of water that is formed or not from surface fluxes. This water may not necessarily be transferred into the permanent thermocline, but instead, may become re-entrained in the seasonal thermocline.
The formation rates calculated from the dynamic and thermodynamic methods for AAIW in the PI and G-SAMW and G-AAIW during the LGM are significantly different and of opposite signs. This suggests that processes such as mixing and

Figure 5.9: a) Annual average subduction rates over the South Pacific, b) lateral subduction component and c) vertical subduction component in the PI (left column) and LGM (right column). Isopycnals bounding SAMW and AAIW are in black contours.
lateral exchange are the dominant processes affecting the formation. As mentioned earlier, we do not take into consideration lateral exchanges of water in the thermodynamic method. Fluxes of water into and out of the domain may redistribute the buoyancy gains, as shown by the large negative formation rates over the LGM. For example, Sloyan et al. [2010], using present day observations, found enhanced interior mixing north of the SAF, preconditioning the local waters for more effective SAMW formation.

If the dynamic method calculates how much water enters the permanent thermocline then we can compare both methods to estimate how much of a contribution mixing makes. Taking the formation rates from the dynamic method and subtracting the thermodynamic formation rates will yield how much mixing affects SAMW and AAIW. We see that surface fluxes for SAMW are larger than subduction into the permanent thermocline, suggesting that interior mixing mixes out SAMW in the PI (Table 5.1 b and c). However, for AAIW in the PI and G-SAMW and G-AAIW in the LGM, mixing increases the formation/subduction of these water masses (positive mixing rates). Mixing is larger in the LGM, and may be attributed to increased wind stress in the LGM.

To take this one step further, we can estimate how much mixing influences these water masses in the permanent thermocline to 30°S, by subtracting the formation rates from the transports at 30°S (Table 5.1c). Again, mixing during the LGM is larger than during the PI, with G-SAMW and G-AAIW being lost as it is transported equatorward.
5.8 Model limitations

There appear to be two main limitations with the NCAR CCSM3 model that can potentially affect the SAMW and AAIW formation rates presented here. They are related to model mixed layer depth and wind stress. There is a shallow bias in the mixed layer depths within the PI simulation as compared with the present day observations. CCSM3 present day and PI simulations have annual average mixed layer depths in the southeast Pacific greater than 125 m. However, they are significantly shallower the estimates from the World Ocean Atlas climatology [Monterey and Levitus, 1997], where the average mixed layer depth in the southeast Pacific is > 500 m; see also Sloyan and Kamenkovich [2007] and Holte et al. [2012]. The origin of this shallow bias is unclear, but it is likely that a shallow mixed layer in the PI may translate to a shallow mixed layer bias in the model in the LGM. The LGM simulation is initialized from temperature and salinity anomalies from the LGM simulation in CCSM 1.4 to the PI simulation in CCSM3. As noted earlier, the formation of SAMW is critically linked to deep mixed layers equatorward of the ACC. The subduction rate equation is based on the depth of the mixed layer; therefore, a shallower mixed layer may lead to an underestimation of SAMW subduction rates. On the other hand, it is not obvious that the shallower mixed layers in the model LGM are necessarily unrealistic for that period. The deepest mixed layers are displaced equatorward in the LGM, farther from the band of westerly wind stress than in observations. As a result of this displacement, there may be less wind induced convection within the mixed layers, leading to a shallower mixed layer in the LGM.
There is some debate on the strength and position of the Southern Hemisphere westerlies in the LGM in both paleo-observations and models. Changes in the Southern Hemisphere westerly wind stress have been linked to glacial-interglacial changes in thermohaline circulation and changes in atmospheric CO$_2$ concentrations [e.g. Imbrie et al., 1992; Toggweiler, 1999; Toggweiler et al., 2006; Toggweiler and Russell, 2008]. An equatorward shift and/or weakened westerlies are thought to restrict the deep water ventilation leading to a more strongly stratified surface ocean. While a poleward shift and/or increase in the westerly wind stress contributes to and strengthens the upper ocean and deep overturning circulation [Toggweiler and Carson, 1995; Toggweiler and Samuels, 1998; Russell et al., 2006].

A 7-10° equatorward shift of the westerly winds has been hypothesized as a driving force of atmospheric CO$_2$ changes in the LGM [Toggweiler, 1999; Toggweiler et al., 2006; Toggweiler, 2009]. Numerous paleo-climate reconstructions of moisture balance (e.g., pollen, lake levels, glaciers, and clay mineralogy) and oceanic frontal shifts suggest an enhanced Southern Hemisphere westerly wind stress in the LGM [Be and Duplessy, 1976; Prell et al., 1979; Alloway et al., 1992; Shulmeister et al., 2004], and/or an equatorward shift [Markgraf, 1989; Heusser, 1989; Lamy et al., 1998; 1999; Moreno et al., 1999; Prinn et al., 2000; Shulmeister et al., 2004] of the maximum in the wind stress. This shift has been interpreted as bringing more moisture to the dry mid-latitudes of South America.

Nonetheless, there has been some debate on the interpretation of these moisture changes within the literature. In the LGM, the tropics were drier and the mid-latitude deserts were wetter than today [see Farrera et al., 1999; Moreno et al., 1999; Kaplan et
al., 2004; Schaefer et al., 2006]. Recent studies have suggested a reinterpretation of the mechanism behind these paleo-moisture changes. Quade and Broecker [2009] and Cartwright et al. [2011] suggest instead that temperature may be a driver of the moisture changes, rather than a shift in the position of the westerlies. The Held-Soden hypothesis predicts both wetter deserts and drier tropics based on temperature changes [see Held and Soden, 2006], as seen in the paleo-observations [see Farrera et al., 1999; Moreno et al., 1999; Kaplan et al., 2004; Schaefer et al., 2006]. Previous interpretations of an equatorward shift in the westerlies can only explain the wetting of mid-latitude deserts, but not the drying of the tropics in the LGM [Quade and Broecker, 2009]. For a model-proxy comparison of this issue, Wainer et al. [2005] using the CCSM1.4 LGM simulation found an intensification of the westerlies south of 50°S and colder sea surface temperatures suggestive of less moisture influx to South America. Along a band of weaker westerlies from 45°S to 25°S there is an increase of the sea surface temperature gradient, which may explain more wet conditions within the paleo-proxy records [Wainer et al., 2005].

However, from a more mechanistic standpoint, a weakening of the Southern Hemisphere westerlies between the glacial and deglacial as implied by Otto-Bliesener et al. [2006] does not agree well with the large changes seen in atmospheric CO₂ and Antarctic temperatures. In order to reproduce the observed increase in CO₂ and warmer Antarctica temperatures at the glacial terminations, Denton et al. [2010] suggests that there needs to be a fairly large transition during the termination (i.e. an increase in the westerlies during deglacial) to induce these changes. This requires that the westerly winds were relatively weak during the LGM; keeping CO₂ within the deep oceans, while
a stronger westerly wind shift during the deglaical could then allow for this built up CO₂ to escape [Denton et al., 2010]. Peeters et al. [2004], Anderson et al. [2009], and Moreno et al. [2010], using a combination of diatoms and foraminifera infer large changes in the westerly wind stress, with an increase during the deglacial into the Holocene.

Modeling studies using coupled atmosphere-ocean general circulation models (GCMs) do not agree as to the strength and position of the Southern Hemisphere westerly winds [e.g. Kitoh et al., 2001; Kim et al., 2002; Kim et al., 2003; Shin et al., 2003; Williams and Bryan, 2006; Otto-Bliesner et al., 2006]. Studies using atmosphere only GCMs have shown both equatorward and poleward shifts in the winds [Wyrwoll et al., 2000; Dorst et al., 2007]. In an analysis of the Paleoclimate Modeling Intercomparison Project 2 (PMIP2) LGM simulations, Rojas et al. [2008] found weakened glacial westerlies in the South Pacific region in all models except for CCSM3. None of the PMIP2 models show large meridional shifts in the westerlies during the LGM [Menviel et al., 2008].

Inconsistencies in the position of the winds in both observations and models suggest to a couple of possibilities; the models are incorrect, the paleo-observations can be interpreted in different ways and/or a combination of the two. To address the first possibility to gain a better understanding of how well the model compares to the paleo-observations, we compare sea surface temperatures (SSTs) from the MARGO Project (Multiproxy Approach for the Reconstruction of the Glacial Ocean Surface) [Waelbroeck, 2009] with SSTs from CCSM3. This comparison is not, however, straightforward, since there are very few paleo-proxy data in MARGO from the South Pacific between 40 and 60°S. The comparison (not shown), particularly in the southwest
and central Pacific, nevertheless suggests that CCSM3 simulates a temperature change between the modern and LGM conditions of 2-4 °, also apparent in the MARGO reconstruction. Therefore, we can conclude that CCSM3 is probably reproducing LGM sea surface temperatures well.

There are also indications that an equatorward shift or weakening in the westerlies can affect SAMW and AAIW formation. One possibility is that an equatorward shift may better align the westerlies along the outcropping isopycnals of SAMW and AAIW, thereby potentially leading to increased air-sea fluxes, convection, and increased upper ocean subduction. SAMW and AAIW formation are influenced by Ekman transport [Rintoul and England, 2002]; therefore, if the wind stress decreases there could be a decrease in the formation of SAMW and AAIW. With the inconclusive observations and interpretation of the observations and models, we cannot draw conclusions about how the strength and position of the winds changed in the LGM and whether the model used in this study accurately depicts changes in the Southern Hemisphere westerlies. However, we can conclude that the observed strengthening of the winds in this model simulation is only one process leading to the increase in the SAMW and AAIW formation also observed in intermediate-depth paleo-records from the South Pacific [Matsumoto et al., 2002; Nameroff et al., 2004; Bostock et al., 2004; Meissner et al., 2005; Bostock, 2010; Muratli et al., 2010]. Even with these potential model limitations, this study allows us to better understand the factors influencing the properties and formation of SAMW and AAIW.
5.9 Summary and conclusions

This study represents a first attempt to describe SAMW and AAIW properties in the South Pacific in an LGM model simulation and investigate the physical processes controlling their formation. The next step would be to use a suite of models to determine if these formation processes (i.e., wind stress and surface fluxes) vary between models and how they relate to differences in sea-ice and wind stress between the models.

Within this study, we find that G-SAMW and G-AAIW in the LGM simulation are colder and denser than in the PI simulation. G-AAIW is no longer defined by a salinity minimum. Because of this, it is difficult to determine a lower boundary of G-AAIW, which may have significant effects on the total formation rates. We do note, that there is the possibility that no Antarctic Intermediate Water is formed during the LGM. We suspect that increased ice cover, particularly over G-AAIW isopycnals inhibits the air-sea gas exchange and ventilation of G-AAIW and thereby, G-AAIW is not forming with a low salinity signal as seen in the present.

Spatial patterns of surface fluxes are similar between the PI and LGM. However, because of the presence of sea-ice that inhibits air-sea fluxes, heat fluxes entering the surface ocean are significantly different between the PI and LGM. Transformation due to surface fluxes over SAMW in the PI is dominated by heat fluxes leading to a positive formation, while G-SAMW is dominated by freshwater fluxes leading to a negative formation or obduction. As for AAIW in the PI and LGM, transformation slightly includes freshwater fluxes leading to a negative formation or obduction. Formation rates calculated from the thermodynamic method for SAMW are 10.7 Sv and -1.6 Sv for AAIW in the PI. During the LGM, formation rates are negative for both G-SAMW (-
29.7 Sv) and G-AAIW (-2.4 Sv), suggesting a lack of formation of these water masses at the surface. Greater sea-ice cover and therefore, greater melting over the isopycnals of G-SAMW and G-AAIW may be responsible for the larger negative formation rates for both G-SAMW and G-AAIW during the LGM.

Annual mean formation rates calculated from the dynamic method for SAMW and AAIW, increase dramatically between the PI and LGM, from 4.3 Sv to 8.9 Sv for SAMW and 4.3 Sv to 8.3 Sv for AAIW. These formation rates are interpreted as the total amount of water forming in the South Pacific that enters the permanent thermocline. The regions of highest subduction correspond to regions of greatest winter mixed layer depths and wind stress, and have increased lateral transports at the base of the mixed layer. Our results of greater formation from the dynamic method for G-SAMW and G-AAIW in the LGM agree well with the limited paleo-proxy data available [Lynch-Stieglitz et al., 1994; Matsumoto et al., 2002; Meissner et al., 2005; Muratli et al., 2010].

Formation rates calculated via the thermodynamic method are interpreted as the amount of water formed or destroyed solely due to surface buoyancy fluxes, and they do not take into consideration mixing. In contrast, the rates calculated from the dynamic method represent the total amount of water that is subducted into the permanent thermocline and into the subtropical gyre. A comparison of both methods as well as transports across 30°S are used to estimate the amount of mixing needed to supply a positive formation of G-SAMW and G-AAIW to the permanent thermocline and to 30°S. These results suggest that mixing plays a large role in redistributing the buoyancy gain over G-SAMW and G-AAIW. Mixing tends to redistribute SAMW in the PI between the surface and thermocline as isopycnals shoal towards the equator.
Increased subduction (via the dynamic method) of G-SAMW and G-AAIW in the LGM may have implications for the transport of climatically important properties into the interior subtropical gyres and equatorial thermocline. Presently, SAMW and AAIW are the most important global source of O₂ and nutrients to the thermocline and equatorial region [Toggweiler et al., 1991; Russell and Dickson, 2003]. Along with changes in subduction, a decrease in the temperatures of G-SAMW and G-AAIW in the LGM will increase the solubility of both O₂ and CO₂ [Martin et al., 2005]. In this regard, the temperature change in the Subantarctic zone is particularly important as this is the area of greatest CO₂ uptake and transport. A combination of cooler temperatures and larger subduction rates could potentially increase the uptake of CO₂ and O₂ within G-SAMW and G-AAIW. However, if subduction rates are too great, the water masses may not have time to reach equilibrium with the atmosphere and therefore, gas concentrations may actually be lower than expected.

The LGM was characterized by increased iron flux from dust to the upper oceans [Petit et al., 1999; Mahowald et al., 1999]. It has been shown that increased iron supply will reduce the uptake of Si(OH)_4 to NO₃⁻ by diatoms, thereby leaving excess Si(OH)_4 within the surface waters [Brzezinski et al., 2003]. During the LGM there was increased iron input to the Southern Ocean and Antarctica, particularly from dust sourced from Australia and South America [Petit et al., 1999]. There is evidence for a shift in fauna in the equatorial region in the LGM, from coccolithopore dominated to diatom dominated due to excess Si(OH)_4 transported to the equatorial region [Broecker et al., 2000; Harrison, 2000; Matsumoto et al., 2002]. Thus, increased formation of G-SAMW and G-
AAIW may increase the transport of excess iron and silica to the equatorial region, helping to fuel equatorial production in the LGM.

Finally, this study also contributes to understanding potential future changes in SAMW and AAIW. This study finds that formation calculated via the dynamic method increases during the LGM, due to increasing wind stress and winter mixed layer depths, while surface stratification increases from the freshwater flux, tends to inhibit the formation of G-SAMW and G-AAIW. Southern Hemisphere westerly wind stress has increased over the last 20 years towards a more positive Southern Annular Mode [Thompson and Solomon, 2002; Gillett and Thompson, 2003; Fyfe et al., 2007]. Upper ocean stratification is also projected to increase, due to sea-ice melt and warming temperatures [Caldeira and Duffy, 2000]. However, the poleward intensification of the westerlies may counteract or slow the upper ocean stratification [Russell et al., 2006]. These competing processes may have significant implications on the future formation of SAMW and AAIW. If the intensification of the westerlies surpasses the effect of stratification from warming associated with increasing atmospheric CO$_2$ concentrations, then there may be increases in the formation of SAMW and AAIW in the future.
Chapter 6

Conclusions and Future Work

Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW) play an important role in the Earth's heat, freshwater and carbon budgets, and ventilation of the Southern Hemisphere subtropical gyres. SAMW and AAIW are large volume relatively cool water masses that sequester significant quantities of atmospheric gases, e.g. CO$_2$ and O$_2$ in their formation regions [e.g., Sabine et al., 2004; Mikaloff-Fletcher et al., 2006]. The second largest sequestration and storage of anthropogenic CO$_2$ in the world’s oceans lies between 40 and 60°S, due to the formation of SAMW and AAIW.

Due to their large volumes, high gas concentrations and a connection to each ocean, SAMW and AAIW can play an important role in regulating and modifying the uptake and storage of CO$_2$ on various climate relevant time scales. This thesis set out to explore four objectives, outlined in Chapter 1, to better understand SAMW and AAIW during the past (Last Glacial Maximum) and present in order to better address future changes of SAMW and AAIW. Conclusions and future work for each chapter are described below.

1. *Estimate rates of formation for SAMW and AAIW in the southeast Pacific, and their inter-oceanic transports using a combination of World Ocean Circulation Experiment (WOCE), Climate Variability and Predictability (CLIVAR), and recently collected hydrographic and chlorofluorocarbon (CFC) data in the southeast Pacific (SAMFLOC). This work is published in Deep Sea Research [Hartin et al., 2011].*
The work presented in Chapter 2 successfully calculated formation rates of SAMW and AAIW in the South Pacific using CFC-12 inventories. In order to accurately calculate formation rates, winter time observations of CFC saturations are needed. This study documented the first winter time observations of CFC-11 and CFC-12 saturations within SAMW (94% and 95%) and AAIW (60%, north of the SAF) from the southeast Pacific. The CFC-12 inventory maps provide a picture of the areas of formation of SAMW and AAIW, with the primary region of formation for SAMW and AAIW being the southeast Pacific. Higher CFC-12 inventories in eddies in the central Pacific are suggestive of the contribution of eddies to formation of SAMW and to a lesser extent for AAIW. The CFC-12 inventories are used to calculate formation rates for SAMW at $7.3 \pm 2.1$ Sv and $5.8 \pm 1.7$ Sv for AAIW that circulate within the South Pacific subtropical gyre.

In order to estimate how much newly formed SAMW is transported from the southeast Pacific to the Atlantic through the Drake Passage, we calculated geostrophic transports across 77°W. A transport of 4.4 Sv of newly formed SAMW is found leaving the South Pacific and entering the Drake Passage. Therefore, the total formation rate of SAMW in the South Pacific is $11.7 \pm 2.2$ Sv. The AAIW formation rate of $5.8 \pm 1.7$ Sv is a lower bound on the formation of AAIW within the South Pacific, as we cannot estimate the volume transport of newly formed AAIW through the Drake Passage. These CFC-derived formation rates represent the average water mass formation rates over the period from 1970 to 2005, and take into account all formation processes, including eddies, winter convection, and mixing. These formation rates help lead to the conclusion that SAMW and AAIW formation in the
South Pacific represents a major portion of the mode and intermediate water formation worldwide. This study provides a multi-decadal average of SAMW and AAIW formation rates, providing a baseline with which to compare formation rates from observations and models from both the past and future climates.

Future work:

This study, while fairly conclusive in calculating formation rates of SAMW and AAIW in the South Pacific, leaves a few areas for further research on this topic.

A) Transport into the Drake Passage of newly formed AAIW was not able to be calculated based on the data set used in this study. There is significant recirculation of AAIW within the ACC that makes it difficult to accurately separate out newly formed AAIW. However, with the addition of floats and increased observations in the southeast Pacific near the Drake Passage, it may be possible to calculate transports. AAIW is traceable not only as a salinity minimum but also as an oxygen maximum. Therefore, using a combination of salinity and oxygen measurements from the southeast Pacific toward the Drake Passage, it may be possible to follow the newly formed AAIW into the Drake Passage. Naviera Garabato et al. [2009] found significant variability in properties of AAIW from the South Pacific, in the Drake Passage and into the southwest Atlantic due to natural variability (i.e., Pacific Decadal Oscillation, El Nino Southern Oscillation and Southern Annular Mode).

B) Mesoscale eddies in the South Pacific were found to be an important contributor to the CFC inventories and therefore, the formation rates of SAMW. Eddies are
widely believed to be the main vehicle of the meridional tracer transport in the Southern Ocean [i.e., Karsten et al., 2002; Lachkar et al., 2007]. A rough estimate done by removing two to three CFC-12 enriched eddies from the inventory calculation, decreased the total inventory by approximately 5%, or each eddy decreased the inventory by about 2% and an approximate 0.1 Sv change in the formation rate. Therefore, depending on the number of eddies shed per year related to the Antarctic Circumpolar Current (ACC), the East Australian Current (EAC), and the influence of the Campbell Plateau, eddies could be making a significant contribution to the formation and properties of SAMW and to a lesser extent AAIW. Future work would be to quantify a yearly flux of eddies shed into the South Pacific in order to better understand how eddies contribute to the formation of SAMW and AAIW.

Future global warming scenarios suggest an enhancement of the Southern Hemisphere westerly winds due to an increase in the intensity and frequency of the Southern Annular Mode [Tsonis et al., 2005; Fyfe et al., 2007]. An increase in wind stress is thought to yield an increase in eddy activity along the ACC [Meredith and Hogg, 2006]. Therefore, understanding how mesoscale eddies influence the formation of SAMW and AAIW are a key to understanding future changes in these water masses.

2. Conduct a Southern Hemisphere assessment of CFC uptake within the National Center for Atmospheric Research (NCAR) Community Climate System Model version 4 (CCSM4). This work is published in part in [Weijer et al., 2012].
Chapter 3 is a part of a large collaborative project conducted to analyze the Southern Hemisphere Oceans within the NCAR-CCSM4 compared to observational data. In particular, my contribution to this project was to investigate CFC concentrations between observations and the model across all three ocean basins. Differences between the model and observed temperature, salinity, potential vorticity, winter mixed layer depth, and CFC concentrations are used to validate the formation and ventilation of SAMW and AAIW in CCSM4. The largest differences between the model and observations across all three ocean basins are within the lower thermocline and intermediate waters. The underestimation of the uptake of CFCs within the model, particularly within SAMW and AAIW isopycnals may suggest inadequate ventilation of these water masses. These differences between the model and observations also suggest biases within the model parameterization. Recent studies have suggested that eddies, turbulent mixing, ocean stratification, and mesoscale processes influence the formation and properties of SAMW and AAIW [Sallee et al., 2008; Sloyan et al., 2010; Herraiz-Borreguero and Rintoul, 2011; Hartin et al., 2011]. A more thorough comparison of the CCSM4 simulation of SAMW and AAIW is conducted in Chapter 4 to begin to understand which of these processes may be responsible for the underestimation in CFC concentrations between the model and observations.

Higher model CFC-11 concentrations, south of the Antarctic Circumpolar Current (ACC) in the Indian and Pacific sectors between the surface and 2000 m, may be due to deficiencies in the representation of Southern Ocean overturning circulation, particularly the upwelling of CFC-free Upper Circumpolar Deep Water (CDW) [Sloyan and Rintoul, 2001a]. Less CDW upwelling allows for the near-surface ocean buildup of CFCs, which
are not diluted by the CFC-free CDW. Bottom waters in all three basins are lower in the model. Assuming that the model is adequately forming AABW [Danabasoglu et al., 2011], then there is the possibility that there is too much mixing of AABW downstream with its surroundings. This suggests that the model may underestimate the sequestration of heat, CO$_2$, and other properties to the interior ocean. These studies of model and observational comparisons are particularly helpful for understanding the physical mechanism responsible for their differences.

Future work:

A) This study conducted a thorough comparison of Southern Hemisphere ocean processes in CCSM4 compared to ocean observations. Future work to expand on this model – data comparison would entail investigating CFC uptake and transport within the Northern Hemisphere oceans. The largest sink of anthropogenic gases, i.e., CO$_2$ and CFCs, is in the North Atlantic [Willey et al., 2004; Sabine et al., 2004] due to the formation of North Atlantic Deep Water. Therefore, it is particularly important in understanding how well the model reproduces the uptake and transport of CFCs in the North Atlantic Ocean.

B) It would also be useful to compare transects through the North Pacific Ocean, and in particular investigating North Pacific Intermediate Water (NPIW) with the model-data comparison. NPIW, like AAIW is characterized by a low salinity signal and acts as a sink of anthropogenic CO$_2$ into the ocean interior.
3. Estimate rates of formation of SAMW and AAIW in the southeast Pacific within NCAR-CCSM4 to compare to the observations in Hartin et al. [2011]. This work was submitted in July 2012 to the Geophysical Research Letters [Hartin et al. submitted].

The Weijer et al. [2012] paper conducted a comparison of observations and model output within the Southern Hemisphere of all three oceans. This work focused on a hemispheric representation of the model, rather than understanding each water mass in detail. Hartin et al. [submitted] conducted a detailed analysis of SAMW and AAIW to compliment the work presented in Weijer et al.[2012].

Comparisons of CFC-12 inventories and formation rates of SAMW and AAIW from observations and model output are important for validating CCSM4. CCSM4 accurately depicts the southeast Pacific as the main region of formation for SAMW and AAIW. However, inventories and formation rates of SAMW in the South Pacific in CCSM4 for 2005 are significantly less than 2005 observations. These differences are potentially due to a shallow bias in the model mixed layer depth and insufficient meridional transport of high CFC waters into the interior. The inventories and formation rates for AAIW in CCSM4 by contrast, are higher than the observational estimates. This is primarily due to higher model inventories in the southwest Pacific and higher surface concentrations within the isopycnals corresponding to AAIW. Causes for the higher surface concentrations are not clear, but may be related to a combination of a cold bias in sea surface temperatures poleward of 45°S in CCSM4 [Danabasoglu et al., 2011] and insufficient meridional transport of CFC waters.
Differences in the modeled and observed CFC-12 concentrations, saturations, and inventories emphasize the need for further model improvement in ocean-atmosphere exchange and upper ocean parameterizations. They also highlight the need for more hydrographic observations within the southwest Pacific. In the model, reduced meridional penetration of CFCs from the source regions further suggests that CO$_2$ uptake and sequestration also may be underestimated by model simulations.

Future work:

A) As with the formation rates calculated from observations, future work would entail calculating formation rates in CCSM4 within the South Atlantic and Indian Oceans. SAMW and AAIW are connected to each ocean via a super gyre, and therefore, the formation and properties of these waters masses are presumably linked. It would be useful to understand how well the model reproduces formation rates of SAMW and AAIW in the Atlantic and Indian Oceans, and to see if the biases in the model found within the South Pacific are widespread across all three oceans. Weijer et al. [2012] compared CFCs in all three oceans, but did not do a detailed study on formation rates.

B) Another important component to investigate is the change in CFC saturations with time. CCSM4 is forced with the atmospheric time history of CFCs. It would be useful to look at the potential variability in CFC saturations at the surface and within the mixed layer. CFC saturations are a key variable in the formation rate calculation. In our calculation, saturation at subduction is assumed constant from one year to the next based on 2005 austral winter observations. Detailed CFC
saturations over time can be used in the formation rate calculation potentially resulting in more accurate rates of formation for SAMW and AAIW.

C) Lastly, formation rates via CFC inventories are one way to calculate formation rates. Another way to calculate formation rates is the dynamic subduction approach discussed in Chapter 5. This method is based on horizontal and vertical velocities at the base of the mixed layer, related to wind stress. These rates can then be compared to work by Sallee et al. [2010] and Karstensen et al. [2002], who have calculated subduction of SAMW in AAIW. It would be useful to also calculate formation rates with this method and compare to the CFC inventory method. In using the dynamic method, velocities would be averaged over the same time frame used in the CFC inventory method, from 1970s to 2005. This would allow for a more direct comparison of average formation rates.

4. Assess the physical mechanisms (i.e. buoyancy fluxes and subduction) responsible for the changes in SAMW and AAIW during the Last Glacial Maximum (LGM), using the National Center for Atmospheric Research (NCAR) Community Climate System Model version 3 (CCSM3), focusing on changes between the preindustrial (PI; ~1850 A.D.) and LGM on SAMW and AAIW in the South Pacific.

This study represents a first attempt to describe SAMW and AAIW properties in the South Pacific in an LGM model simulation and investigate the physical mechanisms controlling their formation. Our results of greater formation (via dynamic method) for G-SAMW and G-AAIW in the LGM agree well with the limited paleo-proxy data available
Formation rates calculated via the thermodynamic method are interpreted as the amount of water formed or not solely due to surface buoyancy fluxes, and they do not take into consideration interior mixing. In contrast, the rates calculated from the dynamic method represent the total amount of water formed and subducted into the permanent thermocline and into the subtropical gyre. A comparison of both methods as well as transports across 30°S are used to estimate the amount of mixing needed to supply a positive formation of G-SAMW and G-AAIW to the permanent thermocline and to 30°S. These results suggest that interior mixing plays a large role in redistributing the buoyancy gain over G-SAMW and G-AAIW. Interior mixing tends to mix out SAMW in the PI between the surface and thermocline.

Increased subduction of G-SAMW and G-AAIW in the LGM may have implications for the transport of climatically important properties into the interior subtropical gyres and equatorial thermocline. Presently, SAMW and AAIW are the most important global source of O$_2$ and nutrients to the Southern Hemisphere thermoclines and equatorial regions [Toggweiler et al., 1991; Russell and Dickson, 2003]. Along with changes in subduction, a decrease in the temperatures of G-SAMW and G-AAIW in the LGM will increase the solubility of both O$_2$ and CO$_2$ [Martin et al., 2005]. In this regard, the temperature change in the Subantarctic zone is particularly important as this is the area of greatest CO$_2$ uptake and storage. A combination of cooler temperatures and larger subduction rates could potentially increase the uptake of CO$_2$ and O$_2$ within G-SAMW and G-AAIW.
Finally, this study also contributes to understanding possible future changes in SAMW and AAIW. Southern Hemisphere westerly wind stress has increased over the last 20 years towards a more positive Southern Annular Mode [Thompson and Solomon, 2002; Gillett and Thompson, 2003; Fyfe et al., 2007]. Upper ocean stratification is also projected to increase, due to sea-ice melt and warming temperatures [Caldeira and Duffy, 2000]. However, the poleward intensification of the westerlies may counteract or slow the upper ocean stratification [Russell et al., 2006]. These competing processes may have significant implications on the future formation of SAMW and AAIW. If the intensification of the westerlies surpasses the effect of stratification from warming associated with increasing atmospheric CO₂ concentrations, then there may be increases in the formation of SAMW and AAIW in the future.

Future work:

A) Future directions for this work would be to use a suite of coupled climate models, particularly the Paleoclimate Modeling Intercomparision Project Phase 3 (PMIP3) simulations to determine if these formation processes investigated in this study (wind stress and surface fluxes) vary between models and vary in response to differences in sea-ice and wind stress between the models. This will allow for a better understanding of the important processes influencing SAMW and AAIW, in hope of better understanding future changes to these water masses.

a. This study shows the importance of properly simulating sea-ice cover and westerly wind stress in order to understand the formation and circulation of SAMW and AAIW under glacial conditions. What metrics of SAMW and AAIW would be needed for this comparison across PMIP3 models?
i. Potential vorticity minimum and deep mixed layers to define SAMW.

ii. Salinity minimum to identify AAIW.

iii. If this salinity minimum is based upon sea-ice extent it would be interesting to compare sea-ice cover in each model with the low salinity signal.

iv. Southern Hemisphere westerly wind stress strength and location. Subduction is directly and indirectly related to the strength of the winds, therefore, this may play a significant role in the rates of SAMW and AAIW.

B) Another useful study would be to investigate G-SAMW and G-AAIW in the South Atlantic. In the LGM simulation of CCSM1.4, G-AAIW in the South Atlantic was still characterized by a salinity minimum (personal communication Ilana Wainer, 2010). A few studies suggest that AAIW was a consistent water mass but may not have been well ventilated during the LGM, due to sea-ice extent or a decrease in the westerly wind stress [Makou et al., 2010; Hendry et al., 2012]. It would be interesting to investigate SAMW and AAIW in CCSM4, as well as calculate formation rates in the South Atlantic.

6.1 Synthesis of methods and model improvement:

a) CFC inventories:

CFC inventories are a useful tool to calculate average water mass formation rates for water collected prior to 2006. After this time, the CFC-12 atmospheric time history curve begins to overturn on itself thereby making the calculation of ages (needed for
inventory method) more difficult. CFCs enter the surface ocean via air-sea gas exchange and are inert in oxygenated waters. Therefore, CFCs can be used as tracers of water mass circulation and formation. The inventory maps reveal the large-scale circulation and regions of greatest air-sea transfer. The total inventory is directly related to the formation rate of a water mass. CFC inventory rates are independent of methods used, i.e. subduction rates, models, inverse methods. These rates represent the average water mass formation rate over several decades (1970-2005).

b) **Dynamic method:**

The dynamic method calculates the total amount of water irreversibly passing through the mixed layer and into the permanent thermocline. This is defined as the downward velocity of a parcel of fluid relative to the base of the mixed layer. The method takes into account the vertical and lateral velocities at the base of the deepest mixer layers, typically found in winter. The subduction rates are integrated across the ocean to obtain a formation rate in Sv.

c) **Thermodynamic method:**

The thermodynamic method is the total amount of water in a particular density class that is formed through buoyancy exchanges between the ocean, atmosphere and sea-ice. Water passes laterally across the outcropping isopycnals at the surface. The convergence of this transformation flux due to air-sea-ice fluxes, yields a formation of water in the particular density surface. This newly formed water may not be transferred to the permanent thermocline, but may be recirculated within the seasonal thermocline.

6.1.1 **List of model improvements:**

This is a list of a few of the model improvements that would potentially improve SAMW and AAIW formation within the model.
1. Mixed Layer Depth: Mixed layers are consistently underestimated, particularly in the Southern Ocean. Within observations SAMW is formed within deep mixed layers in the southeast Pacific. More accurate mixed layers may allow for SAMW to be properly simulated in the model.

2. Potential Vorticity Minimum: Potential vorticity is a measure of the stratification of a water mass. The more convection and mixing within the water mass the lower the potential vorticity. SAMW is characterized by a potential vorticity minimum. SAMW picks up this potential vorticity minimum from intense convection within deep mixed layers. The PV minimum in the model is not as strong and does not penetrate as far into the gyre as observations.

3. Cold SST Bias: CCSM4 has made significant improvements with decreasing the cold SST bias in the Southern Hemisphere. However, the cold SST bias between 45 and 60°S in CCSM4 still exists. This has significant implications for the air-sea gas transfer of CFCs within the model. There is a 4% per degree C change in CFC saturations. Improving this cold bias may lead to a more accurate simulation of AAIW in the model.

4. Eddy Parameterization and Meridional Transport: Currently, in CCSM4, sub-grid scale eddies are parameterized using the Gent-McWilliams scheme. This assumes that eddies remove the potential energy from the mean flow. Therefore, eddies are not explicitly resolved in this model. It has been suggested that eddies are the main vehicle of tracer transport into the interior ocean. This is apparent in Chapter 2 in observations (Figure 2.6). If eddies are resolved, the uptake and transport of CFCs by SAMW and AAIW may be simulated more realistically.
5. Increased Resolution: In order to simulate eddies and not parameterize; increased resolution of the models is needed. However, this introduces increased costs and run times for the model and typically is only done on a regional scale.

6.2 Thesis conclusions

The overall objective of this thesis was to estimate formation rates and understand the processes influencing changes in SAMW and AAIW properties and circulation under present (observations and model) and LGM conditions (model). The main goal was to provide input for prediction of the role these water masses will have in future climates. As seen in Figure 1.1, there is a band of high anthropogenic inventory of CO$_2$ between 40°S and 60°S, which is due to the formation of SAMW and AAIW. Therefore, these water masses have the capacity to influence future climates by their substantial role in the uptake and storage of CO$_2$.

Can future changes in SAMW and AAIW markedly influence changes in CO$_2$ uptake? While we cannot fully answer this question, this work has made a significant contribution to understanding the problem. Average SAMW and AAIW formation rates were calculated across the South Pacific for the period 1970 and 2005, and they represent the baseline with which future changes in their formation can be compared. Average formation rates were calculated within a global coupled climate model to understand how well the model, being used in the next IPCC assessment report, simulates SAMW and AAIW under present day conditions. This work has also shown how surface fluxes and wind stress (via the dynamic method) affect the formation of SAMW and AAIW differently between the PI and LGM. Increased subduction via the dynamic method
increases during the LGM while surface stratification due to increased freshwater flux tends to inhibit the formation of G-SAMW and G-AAIW. This study is particularly important for future understanding of SAMW and AAIW, as it is hypothesized that the competing effects of wind stress and surface stratification will increase under global warming scenarios.
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