Variability in oxygen and nutrients in South Pacific Antarctic Intermediate Water

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[1] Calculation of the initial oxygen based on both phosphate and nitrate data collected along three WOCE transects indicates that the common assumption that new Antarctic Intermediate Water (AAIW) is initially saturated with respect to oxygen is incorrect. The initial oxygen concentration of AAIW is shown to be undersaturated, and the degree of undersaturation varies from year to year. Chlorofluorocarbon data is used to determined the age of AAIW at various latitudes and a frequency analysis of the variability in the initial oxygen concentrations is presented. Possible implications of this variability to the global carbon cycle are suggested. *INDEX TERMS:* 4215 Oceanography: General: Climate and interannual variability (3309); 4504 Oceanography: Physical: Air/sea interactions (0312); 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4845 Oceanography: Biological and Chemical: Nutrients and nutrient cycling; *KEYWORDS:* oxygen, intermediate water, South Pacific Antarctic, WOCE

1. Introduction

[2] The Southern Ocean acts as the lungs of the ocean; drawing in oxygen and exchanging carbon dioxide. A quantitative understanding of the processes regulating the ventilation of the Southern Ocean today is vital to assessments of the geochemical significance of potential circulation reorganizations in the Southern Hemisphere, both during glacial-interglacial transitions and into the future. Traditionally, the change in the concentration of oxygen along an isopycnal due to remineralization of organic material, known as the apparent oxygen utilization (AOU), has been used by physical oceanographers as a proxy for the time elapsed since the water mass was last exposed to the atmosphere. The concept of AOU requires that newly subducted water be saturated with respect to oxygen and is calculated from the difference between the measured oxygen concentration and the saturated concentration at the sample temperature. This study will show, however, that the production of Antarctic Intermediate Water (AAIW) during deep winter convection in the Southern Ocean produces a water mass which is not equilibrated fully with respect to oxygen when it is subducted, implying that the these waters are more recently ventilated than they appear. We also

suggest that the degree of undersaturation may be variable from year to year.

[3] Initial oxygen concentrations are calculated with a Redfield-type analysis from both the phosphate and the nitrate data along three transects from the WOCE cruises, and are shown to be different than the calculated oxygen saturation based on temperature and salinity. Chlorofluorocarbon data is used to create an age model so that the interannual variability in the oxygen saturation of new AAIW can be assessed. A frequency analysis of the variability in initial oxygen is performed and possible physical explanations for the variability are given. Finally, possible implications of this variability to the global carbon cycle are discussed.

2. Background

[4] The South Pacific oxygen maximum is created by the outcropping of subthermocline water in the Southern Ocean where high winds, cold water, and upwelling of oxygen-undersaturated deep water maximize the uptake of oxygen in the surface water [*Talley*, 1996]. The role of the Southern Ocean as a conduit for atmospheric oxygen to enter subthermocline waters in the Pacific has been assessed by detailed inverse modeling of hydrographic data to produce estimates of the flux of oxygen across 30°S [*MacDonald*, 1993]. According to this analysis, the total amount of oxygen fed northward into the Pacific and Indian Oceans by the Southern Ocean wind-driven circu-

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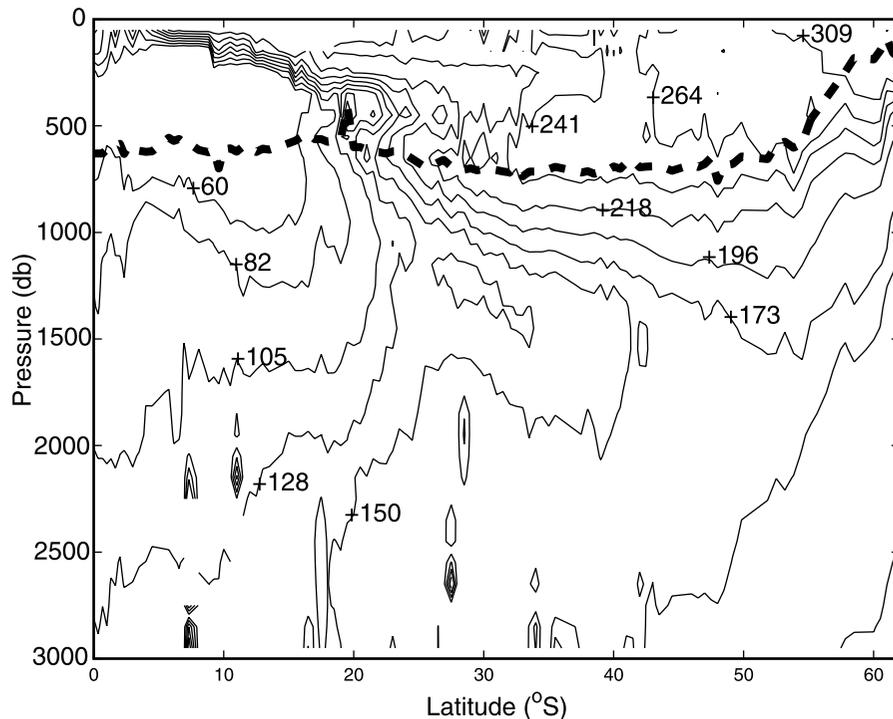[1]Now at Geophysical Fluid Dynamics Laboratory, NOAA, Princeton University, Princeton, New Jersey, USA.

Figure 1. Oxygen concentration (μmol/kg) along the 110°W, P18. The dashed line represents the isopycnal corresponding to the core of Antarctic Intermediate Water (σ_θ = 27.051 above 500 dbar and σ_1 = 31.634 below 500 dbar).

lation (330,000 mol/s and 170,000 mol/s, respectively) dwarfs the amount of oxygen being transported southward into the Southern Ocean by North Atlantic Deep Water (90,000 mol/s).

[5] The Ekman drift in the surface layer of the Southern Ocean between the Polar and Subantarctic Fronts is substantial due to the extreme high westerly winds over the Southern Ocean, especially during winter. This northward drift in the surface waters creates a divergence on the Polar Front and large areas of upwelling water from deep in the water column [*Whitworth et al.*, 1982]. In addition, large amounts of rain accumulate in the surface waters during their drift northward, lowering the salinity of the water. The low-salinity Southern Ocean surface waters are subducted when they reach the Subtropical Front because they are significantly colder and therefore denser than the surface waters of the subtropical gyre. The subducted Southern Ocean surface waters mix across the Subtropical Front forming Subantarctic Mode Water and Antarctic Intermediate Water, the building blocks of the global ocean's shallow-overturning circulation.

[6] As with most water masses subducted in frontal processes, the bulk chemical properties of Antarctic Intermediate Water are determined primarily by the properties of the water subducted in late winter when the surface water is coldest. This winter water escapes below the thermocline as the position of the thermocline in the water column shoals due to seasonal warming [*Woods*, 1985]. In most areas of the ocean, the winter water subducted is of fairly constant composition because the density of the water subducted is

similar from year to year. If the water has enough time to equilibrate fully with the atmosphere and if the biological production of oxygen in the winter is low, the oxygen composition will also be fairly consistent because the temperature of the water will determine the amount of oxygen subducted with the water mass.

[7] In the Southern Ocean, the wind controls the concentration of oxygen in water subducted during the winter in two ways. First, the wind affects the amount of time a water parcel spends at the surface by determining the rate of Ekman transport and the extent of turbulent mixing in the surface layer. Second, the rate at which oxygen is exchanged between the surface water and the overlying atmosphere is determined by the wind stress and the deviation of the surface oxygen concentration from saturation [*Wanninkhof*, 1992]. The wind influences the waters' degree of undersaturation with respect to oxygen (see Figure 1 for the meridional distribution of oxygen with depth), because of a large latitudinal gradient in oxygen concentration south of the Polar Front (65°S − 60°S). The oxygen gradient is pronounced, even though the vertical gradient in temperature is small, creating the possibility that water upwelled along outcropping isopycnals could have dramatically variable oxygen concentrations (squares, Figure 2a).

[8] Biology, although significant in determining the oxygen content of surface waters globally, is probably not significant in determining the initial oxygen concentration of AAIW formed in the winter due to the weak solar forcing and weak biological activity at the time when these waters
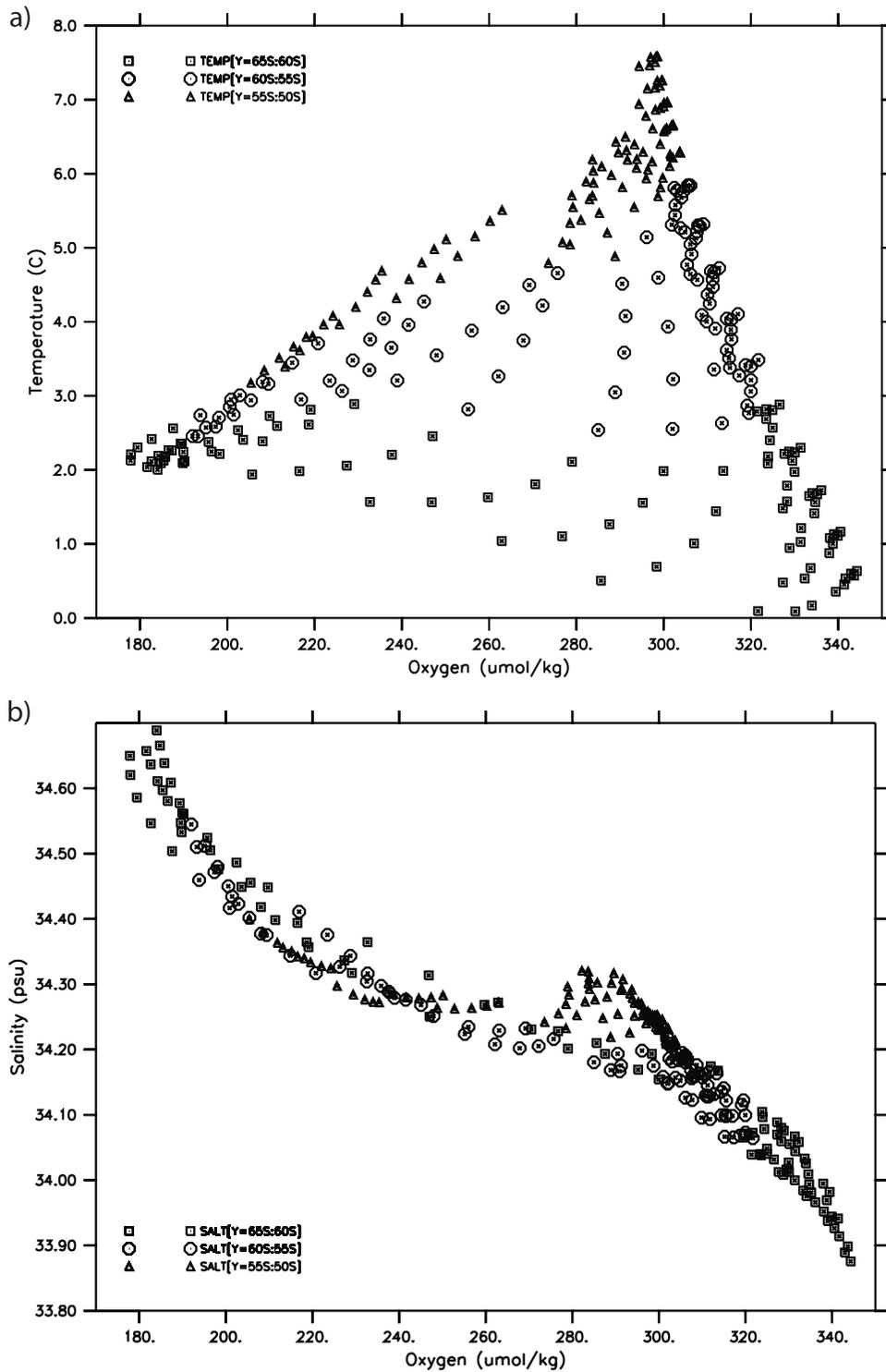
Figure 2. Plots of (a) temperature and (b) salinity versus oxygen content at 110°W between 65°S and 50°S and between 1000 m and the surface. Squares are data between 65°S and 60°S; circles are data between 60°S and 55°S, and triangles are data between 55°S and 50°S. Data are from the World Ocean Atlas 1998 [*Conkwright et al.*, 1998].
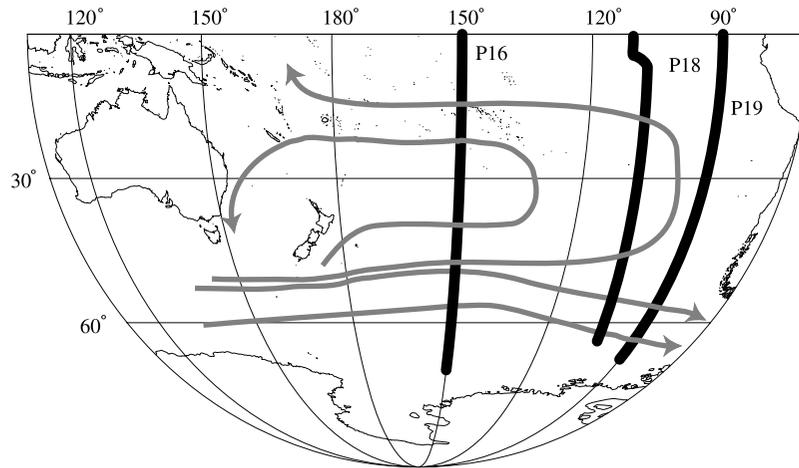
Figure 3. Map showing the flow of Antarctic Intermediate Water in the South Pacific [after *Reid*, 1985]. Also shown are the locations of WOCE Hydrographic Program transects P16, P18, and P19 along 150°W, 110°W, and 90°W, respectively.

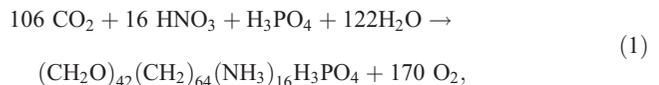are subducted. The effects of biology on the initial concentration of oxygen in AAIW will be neglected here.

3. Redfield Analysis of Initial Oxygen

[9] There have been numerous efforts to quantify the degree to which the concept of a "Redfield ratio" holds: where in the ocean it might fail, to what degree, and why. The broad consensus is that the respiration coefficient ($\Delta O_2/\Delta PO_4$) is universal in the ocean, regardless of region or depth of the isopycnal surface [*Anderson and Sarmiento*, 1994; *Peng et al.*, 1987; *Broecker et al.*, 1985; *Takahashi et al.*, 1985]. This study takes a different approach than the traditional focus on the differentiation of water masses and their origins based on their "initial phosphate" concentrations, PO_4^*. This study analyzes the variability in initial oxygen implied by apparent variability in the ratios of both $\Delta O_2/\Delta PO_4$ and $\Delta O_2/\Delta NO_3$, in a particular, easily identifiable, water mass. This strategy is most applicable for water masses formed in the Southern Ocean, where the process of mixing subthermocline waters to the surface produces varying degrees of saturation in subducted water masses [*Piola and Georgi*, 1982].

[10] To determine the effect of the Southern Ocean in the global ocean cycling of oxygen, the observed Antarctic Intermediate Water oxygen concentrations are corrected for changes due to the remineralization of organic material using Redfield-style calculations along isopycnals extending out of the Southern Ocean. This regional analysis of the potential variability of oxygen export from the Southern Ocean to the Pacific involves data from the equator to 65°S from three WOCE transects; P16 at 150°W, P18 at 110°W and P19 at 88°W (Figure 3). By using precise chemical measurements to correct for the effect of remineralization on the chemical composition of water along an isopycnal surface, the longer-term variability of the initial concentration of oxygen in Antarctic Intermediate Water can be examined.

[11] Primary producers in the surface waters take up biologically important components in a predictable ratio first described by *Redfield et al.* [1963] and most recently recalculated by *Anderson and Sarmiento* [1995]. The distribution of P : N : $C_{organic}$: $-O_2$ ingested by phytoplankton in the ocean, as defined by *Takahashi et al.* [1985], is 1: 16: 106: 170, i.e.

$$106\ CO_2 + 16\ HNO_3 + H_3PO_4 + 122H_2O \rightarrow$$
$$(CH_2O)_{42}(CH_2)_{64}(NH_3)_{16}H_3PO_4 + 170\ O_2, \tag{1}$$

where the first term on the right-hand side is the dissolved organic matter (DOM).

[12] Most phytoplankton are consumed and eventually fall through the water column as fecal pellets until remineralized by bacteria. In this reversal of the above equation, nutrients are released and oxygen is consumed. The amount of oxygen consumed is proportional to the amount of dissolved organic material that has been remineralized. Thus, the increase in nutrient concentrations along an isopycnal surface since ventilation can be used to correct the observed oxygen concentration for the effect of the rain of organic material through the water column and subsequent remineralization (equations (2) and (3)). In this study, the mean observed Redfield ratio of phosphate to oxygen and nitrate to oxygen has been used to quantify the cumulative effect of biological productivity in the surface waters and such remineralization processes on the chemical composition of Antarctic Intermediate Water [*Takahashi et al.*, 1985].

[13] The variability in the Redfield ratio of P:N:O was determined by vertically interpolating bottle measurements of phosphate, nitrate and oxygen onto appropriate isopycnal surfaces using a cubic spline. The fit of the spline was examined at every station to ensure that the oxygen maximum corresponding to AAIW was well resolved. Stations missing data at the critical depths encompassing the relevant isopycnals were excluded from the analysis. Isopycnal surfaces were calculated relative to the surface for stations where the isopycnal was found at a pressure above 500 dbar
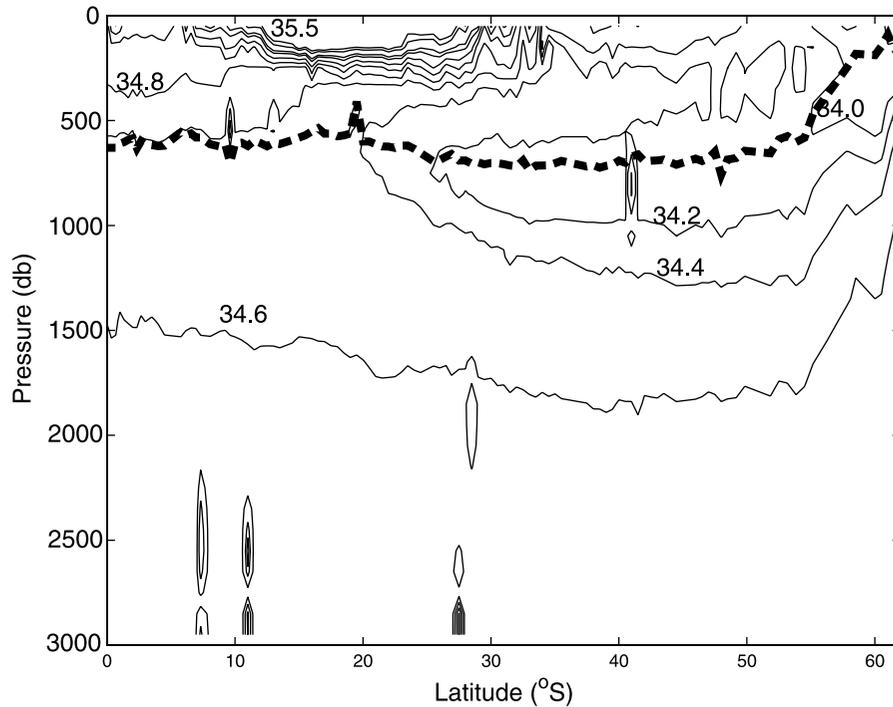
Figure 4. Salinity along 110°W, P18. The dashed line represents the isopycnal corresponding to the core of Antarctic Intermediate Water (σ_θ = 27.051 above 500 dbar and σ_1 = 31.634 below 500 dbar).

and relative to 1000 dbar for pressures below 500 dbar. The isopycnal corresponding to σ_θ = 27.051 above 500 dbar and σ_1 = 31.634 below 500 dbar was chosen as best representing the core of Antarctic Intermediate Water in the South Pacific (Figures 4 and 1). This isopycnal intersects the core of the low salinity and high oxygen tongues in each of the three transects examined and thus should minimize the effects of diffusion on the concentration of phosphate, nitrate and oxygen.

[14] Along the isopycnal on each transect, a least squares fit of oxygen to phosphate concentration and oxygen to nitrate concentration was used to determine the variability in the Redfield ratios. The mean values of the Redfield ratios determined by this calculation were used for subsequent calculations (see Table 1).

[15] After the O$_2$, NO$_3$, and PO$_4$ concentrations were interpolated onto the isopycnal surface corresponding to the core of AAIW in the South Pacific, the values for the three transects were plotted: NO$_3$ against PO$_4$ (Figure 5a), O$_2$ against PO$_4$ (Figure 5b), and O$_2$ against NO$_3$ (not shown). Only those data from the isopycnal north of 50°S were used; south of 50°S, water along the isopycnal showed evidence of mixing and contact with the atmosphere in the form of widely varying oxygen concentrations. The results for the three transects and the results for the sum of the three transects together are summarized in the following table (Table 1).

[16] These results were used to calculate the change in initial oxygen in Antarctic Intermediate Water. The initial oxygen concentration calculated using nitrate is expressed as

$$[O_2]_{initial} = [O_2]_{observed} + 12.4\big([NO_3]_{observed} - 24 \ \mu mol \ kg^{-1}\big), \quad (2)$$

where the Redfield ratio of O$_2$:N is 12.4 and the surface nitrate concentration is estimated from surface waters at 55°S as 24 ± 1 μmol·kg^{-1} (see Figure 5a). The initial oxygen concentration calculated using phosphate is expressed as

$$[O_2]_{initial} = [O_2]_{observed} + 176\big([PO_4]_{observed} - 1.67 \ \mu mol \ kg^{-1}\big), \quad (3)$$

where the Redfield ratio of O$_2$:P is 176 and the surface phosphate concentration, obtained from the assumed surface nitrate value of 24 μmol·kg^{-1} and Figure 5b, is estimated to be 1.67 μmol·kg^{-1}.

[17] Attempts were made to limit the error on the calculation of initial oxygen through several techniques. No measurements that had been flagged for questionable data quality by the principal investigators on the relevant cruises were used. Only stations that had adequate sampling at the required depths were used. Data from three independent transects, each with at least 120 stations, were examined, but only those stations which had adequate resolution (at least

Table 1. Summary of Redfield Ratio in AAIW[a]

Transect	O$_2$/PO$_4$	O$_2$/NO$_3$	NO$_3$/PO$_4$
P16 - 150°W (78 pts)	186 ± 2	14.8	12.51
P18 - 110°W (113 pts)	187 ± 2	12.3	15.13
P19 - 90°W (95 pts)	175 ± 1	12.9	13.53
Total (286 pts)	176 ± 2	12.4	14.11

[a]Sigma theta = 27.051 above 500 dbar and sigma one = 31.634 below 500 dbar.
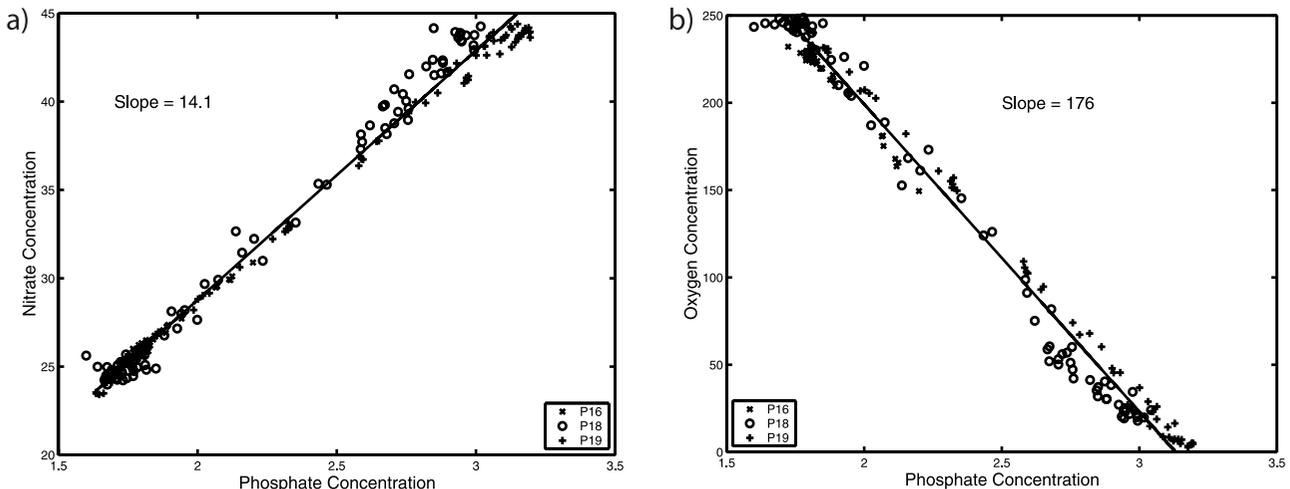
Figure 5. (a) Phosphate to nitrate and (b) phosphate to oxygen Redfield ratios in Antarctic Intermediate Water (interpolated from hydrographic station data).

15 measurements above 1500 dbar) of the AAIW maximum in oxygen were included in the eventual analysis. Two separate measurements, nitrate and phosphate, were used to estimate the initial oxygen concentration, so that the results could be distinguished from noise in the data. Realistic values for surface nutrient concentrations derived from measurements made during the WOCE cruises in the Southern Ocean were used for the calculations and those values were compared with values reported for similar latitudes in the Southern Ocean [*Takahashi et al.*, 1993]. Of the measurements made, 286 total measurements of oxygen, nitrate and phosphate were interpolated onto the Antarctic Intermediate Water isopycnal to generate the Redfield ratios reported here.

[18] The observed oxygen distribution shows the same pattern as it did in the contour plot: high oxygen concentrations south of the Subantarctic Front, decreasing concentrations through the subtropical gyre, and drastically decreasing concentrations as the isopycnal intersects the South Equatorial Current (Figure 1). The two calculations of initial oxygen, using phosphate and nitrate concentrations, are similar in magnitude as well as in phase and amplitude (Figure 6). These two estimates of initial oxygen demonstrate the tight correlation between nitrate and phosphate and the much more variable relationship between either the nitrate or the phosphate and the observed oxygen concentrations (scatter in Figure 5b).

[19] The intermediate waters of the South Pacific, as represented by the three transects analyzed, have lower ratios of nitrate to phosphate than the conventional Redfield ratio of 16 because of the large areas of denitrification present in the eastern and equatorial Pacific. This is best demonstrated by the decoupling of the nitrate- and phosphate- predicted initial oxygen concentrations between 15°S and the equator along 110°W and 90°W, coincident with the observed extreme low in oxygen (Figures 6b and 6c).

[20] The amplitude of variability for P18 (Figure 6b) is greater than that for P16 (Figure 6a) or P19 (Figure 6c). This may be the effect of different mixing regimes repre-

sented along these meridional sections. According to *Reid*'s [1985] assessment of the flow fields in intermediate water (Figure 3), P16, at 150°W, intersects the center of the gyre, P18, at 110°W, intersects the greatest north-south transport and P19, at 90°W, intersects a recirculation along the Chilean and Peruvian upwelling regions. The more direct transport of AAIW from south to north along transect P18 implies a higher amplitude variability from year to year of the initial oxygen concentrations in AAIW.

[21] A possible explanation for the coherent variability in the initial oxygen concentration derived from the ratios of $O_2 : N$ and $O_2 : P$ in Antarctic Intermediate Water could be due to variability in the surface nutrient concentrations. If, however, as *Takahashi et al.* [1993] report, the seasonal nutrient concentrations in the surface waters of the Southern Ocean correspond tightly to the seasonal temperature change, then variability in preformed nutrients during the coldest part of the year is unlikely, especially given that the initial oxygen is calculated along an isopycnal surface where the temperature change is less than 0.4°C between 50°S and 20°S. Changes in the surface nutrient concentrations would have to be due to biologically driven changes in productivity which erode the nutrient concentration of the upwelled waters on the Polar Front. Significant biological changes are unlikely to happen during the rough seas and darkness of October or to have the magnitude required to generate variability of approximately 40 μmol·kg^{-1} in calculated initial oxygen. (A 40 μmol·kg^{-1} change in initial oxygen would require an interannual variability in surface phosphate and nitrate concentrations of 15%.)

[22] Other possible explanations for this observed variability include noise in the data, or eddy propagation. Given the reasonable agreement between the phosphate- and nitrate- calculated pre-formed oxygen values, it is unlikely that experimental error or errors in the fit of the cubic spline at particular stations accounts for the variability. Eddies are possible mechanisms for the variability identified, but the length-scale of the station spacing, 40 km, and the spatial
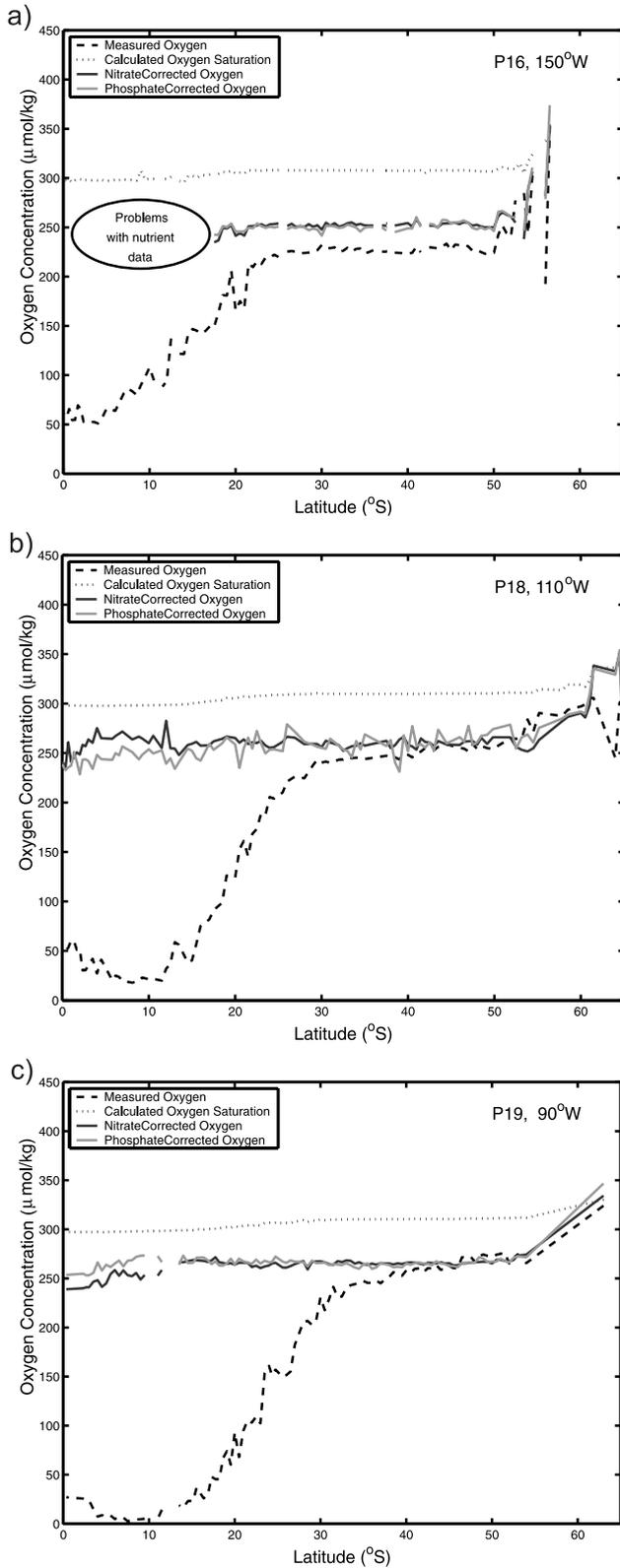
Figure 6. Oxygen concentrations (measured and corrected) in Antarctic Intermediate Water. Stations north of 15°S along P16 were discarded due to either questionable flags from the principal investigator or the lack of sufficient measurements to calculate the value along the isopycnal.

extent of the anomalies, usually two to three stations, makes this explanation also unlikely.

[23] To gain further insight into the possible mechanisms affecting the oxygen variability, this study assesses the possibility of estimating a frequency of the observed variability by first defining an age model appropriate to AAIW on the various sections, and then examining the frequency of the observed variability.

4. Age Model

[24] Using chlorofluorocarbon concentrations to define an age model makes it possible to use small changes in the concentration of oxygen, phosphate and nitrate on an isopycnal surface to produce a record of the variability of initial oxygen concentrations in water subducted in the Southern Ocean and exported as Antarctic Intermediate Water. The ventilation record thus identified may have implications for variability in air-sea gas fluxes, interbasinal nutrient distribution, and equatorial denitrification and production.

[25] Since chlorofluorocarbons (CFCs) were first produced and released into the atmosphere in 1932, F-11 (trichlorofluoromethane, CCl_3F) and F-12 (dichlorodifluoromethane, CCl_2F_2) have been equilibrating with the surface ocean. The dry air mole fractions of F-11 and F-12 have increased exponentially from the 1950s through the mid-1970s and the ratio of their mole fractions has increased linearly (Figure 7). Using P. Salameh and R. Weiss's reconstruction of the Southern Hemisphere atmospheric mixing ratio of F-11 to F-12 since 1932 (Tables of reconstructed atmospheric F-11 and F-12 histories, personal communication, 1992), the year of ventilation of AAIW at each station along the transects can be inferred from the ratio of F-11 to F-12 in the sample (see, e.g., Figure 11) and is called the "ratio age."
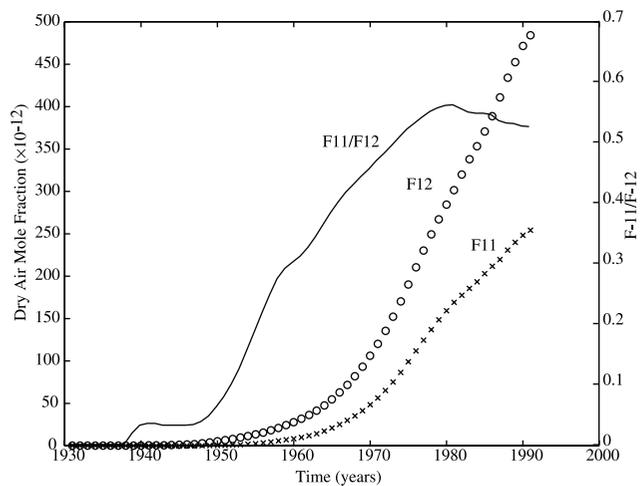

Figure 7. Reconstructed history of the atmospheric dry air mole fraction of F-11 and F-12 in the Southern Hemisphere. Note that the F-11/F-12 ratio does not change greatly after the mid-1970s, thereby greatly increasing the errors in using this ratio as a dating tool during this part of the record.

[26] The ratio age of Antarctic Intermediate Water is calculated by using the solubilities of F-11 and F-12 to estimate the dry air mole fractions of F-11 and F-12 that must have been present when the water was ventilated to produce the ratio of F-11 to F-12 currently present along the isopycnal surface. The seawater concentration (pmol/kg) is proportional to the atmospheric CFC mole fraction following the relationship:

$$C^* = F(\theta, S)x, \tag{4}$$

where C^* is the equilibrium concentration, F is the solubility function of potential temperature, θ, and salinity, S, reported by *Warner and Weiss* [1985], and x is the dry air mole fraction.

[27] The "apparent age" of intermediate water in the South Pacific was determined from this relationship, and from the atmospheric history by assuming that the water mass had survived as a closed and unmixed parcel, or was diluted only by CFC-free water, and then comparing the ratio of the calculated dry air mole fraction for F-11 and F-12 to the reconstructed atmospheric history of the ratio. The "concentration age" is determined for each gas separately and assumes that there was no dilution, so that in the cases where the concentration age is valid it should equal the "apparent age."

[28] The estimated age of a water parcel reflects the mixing of source waters with differing ventilation time-scales and pathways, some potentially quite old [*England*, 1995]. Deviations from the ideal age occur because of difficulties in defining boundary conditions, natural tracer backgrounds and non-linear mixing. In the case of South Pacific AAIW, defining boundary conditions and non-linear mixing are important sources of error in the calculation of the apparent age.

[29] For the calculation of the age in both models, the assumption was made that the water was in equilibrium with the atmosphere and that the air-water interface was saturated with water vapor at a total pressure of 1 atm when the water was last in contact with the atmosphere. Note that this assumption does not agree with the suggestion that initial oxygen concentrations are undersaturated in AAIW: this constitutes a potential error associated with the calculation of the ages for South Pacific AAIW and deviations from the ideal age (the case where the concentration age equals the apparent ratio age) due to boundary conditions are inherent in the hypothesis being tested, namely that the percent saturation with respect to oxygen (or CFCs) in South Pacific AAIW varies over time. Therefore, the assumption that enables the direct comparison of dry air mole fraction with the atmospheric reconstruction may not necessarily hold. Ages derived from this comparison will be older than the ideal age because the water parcel was not at equilibrium at the time of subduction. These deviations from equilibrium could not, however, lead to the patterns of ratio age vs. concentration age seen in Figures 8 and 10.

[30] The solubility of F-11, and therefore its gas exchange rate, is greater than the solubility of F-12 and this effect is exacerbated when the gas transfer velocities are high. Although the gas transfer velocities of F-11 and F-12 have
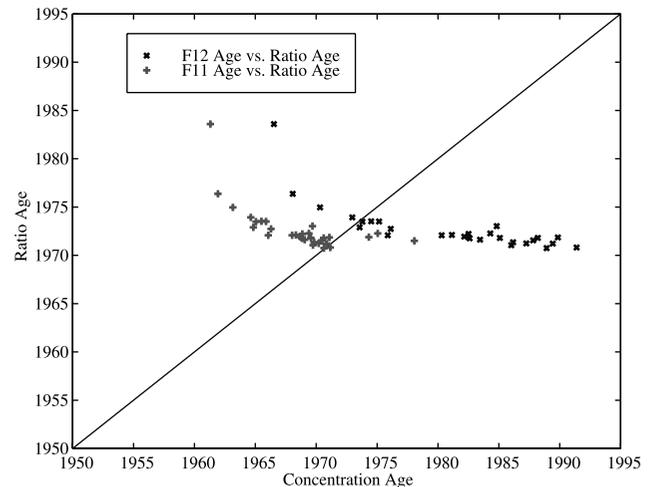

Figure 8. Concentration age verus ratio age along 150°W, P16 in AAIW. Ratio ages do not reflect plausible production scenario, indicating mixing with older waters. The locus for the ideal case in which the concentration ages equal the ratio age is plotted as a solid line.

not been measured at wind speeds higher than 10 m/s, the effect of wintertime winds in the Southern Ocean (12–18 m/s) can be assumed to add to the underestimation of the apparent age of the subducted water. Undersaturation at the time of subduction, however, will affect the ratio age less than the concentration age. The relative undersaturation for each gas depends on its gas transfer velocity which depends on its Schmidt number. The gas transfer velocities for F-11 and F-12 differ by about 4% so their relative undersaturation will be roughly equal. The concentration age, on the other hand, is much more sensitive to undersaturation.

[31] Water exported from the Southern Ocean does not move directly from south to north along an isopycnal surface: the current meanders from east to west and around the subtropical gyre (Figure 3). Any attempt to address the time-varying composition of a water mass must consider this circuitous path; thus the time since ventilation will vary nonlinearly along a meridional isopycnal surface. Intermediate water isopycnals in the South Pacific have been shown to outcrop around 55°S in winter [*Reid*, 1985]. The core of low salinity water extends counterclockwise around the center of the subtropical gyre and turns westward at approximately 16°S (Figure 3).

[32] To demonstrate the age distribution and limited potential source region for the South Pacific tongue of Antarctic Intermediate Water, the individual concentrations of the chlorofluorocarbons, F-11 and F-12, as well as their ratios, were used to derive age models along 150°W, 110°W and 90°W (Figures 8, 9, and 10). The ratio ages do not predict plausible age models along 150°W or 90°W, indicating that AAIW along these transects has been mixed with older waters. AAIW along 110°W does not seem to show this behavior. One possible explanation for this difference between the mixing regimes along 150°W, 110°W, and 90°W may be that the transect along 150°W intersects the center of the gyre and that the transect along 90°W
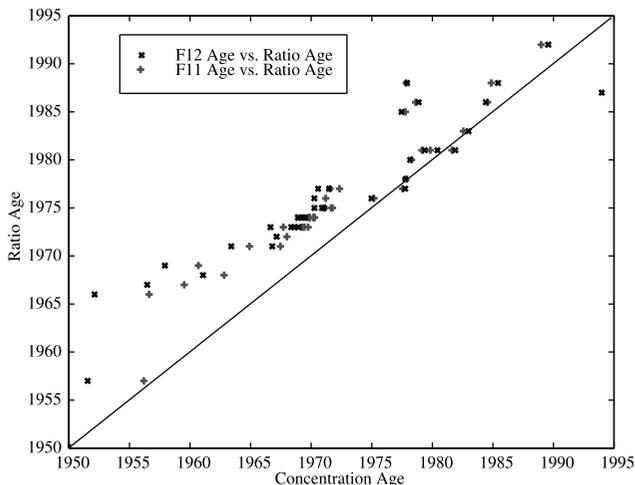
Figure 9. Concentration age versus ratio age along 110°W, P18 in AAIW. Both concentration ages and ratio ages predict a plausible production scenario for AAIW, indicating a lack of mixing with older waters.

intersects a recirculation along the Chilean and Peruvian upwelling regions. Another explanation is that the F-11/F-12 ratio stopped increasing after about 1974 and both P16 and P19 had little water older than this. The transect along 110°W (P18) may thus provide a more direct transport of intermediate water from south to north.

[33] Along 110°W, the recently ventilated water in the Southern Ocean has quite high concentrations of CFCs which decrease with latitude to 10°S where they are no longer detectable (Figure 11a). The ratio ages along this transect indicate that the year the water was ventilated decreases from the Subantarctic Front (about 45°S) where the water appears to have been ventilated in 1985 (although the F-11/F-12 ratio changes less after about 1975, so dates more recent this are subject to higher uncertainty) to the recirculation of the South Equatorial Current (about 10°S), where the water appears to have been ventilated prior to 1955 (Figure 11b). These distributions corroborate Reid's original assumptions regarding the flow pattern of Antarctic Intermediate Water in the South Pacific, as well as pointing out the unlikelihood of there being another water mass, more recently ventilated, that would complicate the interpretation of the calculated initial oxygen values.

[34] Transient tracer-derived ages have a maximum apparent age set by the time since the introduction of the tracer into the ocean and are weighted toward the components with the greatest tracer loading, in this case, the youngest waters. The apparent tracer age of a mixture of two water parcels along the isopycnal surface will be younger than the linear average of the two original ages. Non-linear mixing effects become more severe for older waters where the water parcel ages approach the age at which the underlying assumptions used to implement the tracer method break down. In the case of South Pacific AAIW, the age model calculated from the ratio of F-11 and F-12 will underestimate the age of the water on the isopycnal because of mixing with older waters and that underestimation will

become more severe at stations farther from the source region of the water mass in the Southeast Pacific.

5. Frequency Analysis

[35] The most energetic modes in initial oxygen concentration were reconstructed by using a singular spectrum analysis (SSA) [*Vautard et al.*, 1992] of the time-varying phosphate and nitrate-corrected oxygen concentrations (Figure 12). The data were subsampled at regular intervals using a cubic spline interpolation and then the long-term trend was removed from the record. Using a window-length of 20 years, two modes emerge, one with a period of 1.8 years and one with a period of 4.9 years. Monte Carlo simulations suggest that these modes represent statistically significant (at the 95% confidence level) concentrations of variance. This analysis was carried out using the software package of *Paillard et al.* [1996].

[36] The first component of the variability is possibly an interannual variability aliased to a lower frequency (1.8 years) that may be associated with the changes in the formation processes of Antarctic Intermediate Water. Although water subducted as the coldest time of the year is relatively consistent in salinity and temperature [*McCartney*, 1977], the amount of oxygen subducted with that water appears from this analysis to be variable from year to year. The second mode of variability has an time period of approximately 5 years. This variability may be associated with the circulation of the Antarctic Circumpolar Wave, a warm sea-surface temperature anomaly often associated with a subsequent decrease in wind speed, which propagates around the Southern Ocean with the Antarctic Circumpolar Current and has a period of about 4 years [*White and Peterson*, 1996].

[37] The frequency analysis employed was only possible for the most densely sampled transect, P18 at 110°W. The other transects did not have an adequately dense distribution of precise measurements at the appropriate density surface. Given the flaws in the age model, any estimation of the
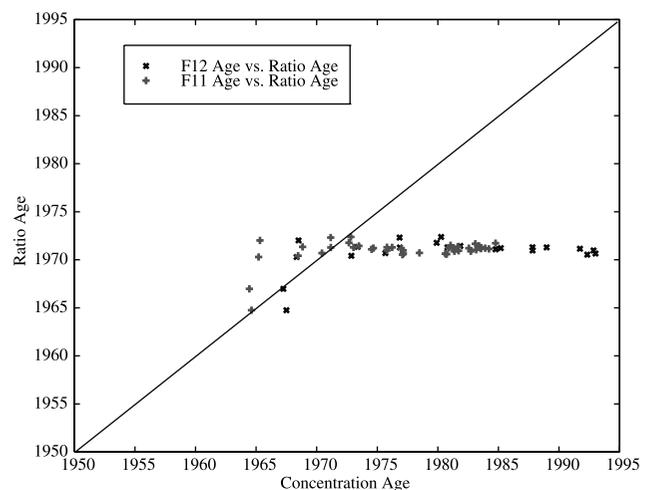

Figure 10. Concentration age versus ratio age along 90°W, P19 in AAIW. Ratio ages do not reflect plausible production scenario, indicating mixing with older waters.
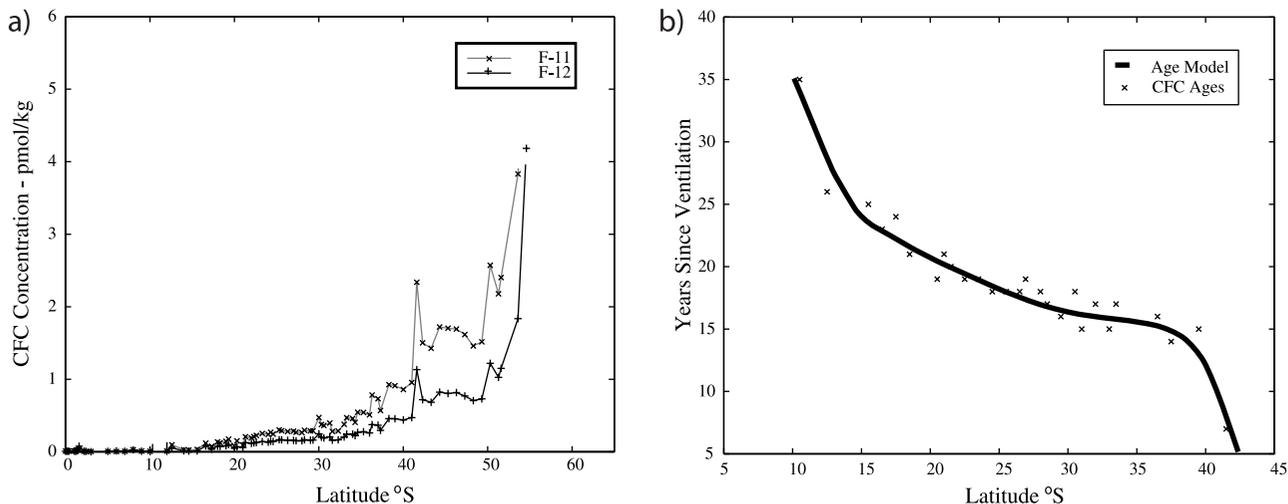
Figure 11. (a) Chlorofluorocarbon concentrations, F-11 and F-12, in Antarctic Intermediate Water along 110°W, P18 (interpolated from hydrographic station data). (b) Age model based on the ratio of the concentrations of F-11 to F-12.

frequency of the variability of initial, or preformed, oxygen must be considered tenuous at best. Of the possible errors associated with the age model, changes in the percent saturation of the subducted water parcel are the most likely to affect the frequency analysis. Using a smoothed curve fitted to the ratio ages calculated at each station, however, precludes the introduction of this short-term variability. Rather, the errors associated with the age model would tend to attenuate the reconstructed oxygen signal with time, possibly explaining the "interannual" variability with a 1.8-year time period.

6. Discussion and Implications

[38] The distributions and temporal evolution of transient tracer fields in the ocean can potentially provide a wealth of information about the process by which the ocean is ventilated on timescales ranging from months to decades. In practice, however, difficulties arise from limited spatial and temporal sampling of the tracer fields, uncertainties in the historical surface boundary conditions (both oceanic and atmospheric) and ambiguities in the derived circulation fields. It is possible that the variability in preformed oxygen in South Pacific AAIW is the result of the wind-driven upwelling circulation in the Southern Ocean.

[39] Two frequencies of variability were observed in the record of the change in initial oxygen with a change in time along 110°W. The dominant variability may be an aliased interannual variability, possibly associated with the interannual changes in the formation processes of Antarctic Intermediate Water. The second, less pronounced, frequency is an oscillation with about a 5-year time period. It is possible that this oscillation is due to the sea surface temperature anomalies documented by *White and Peterson* [1996] and *Jacobs and Mitchell* [1996]. These anomalies propagate eastward around the Antarctic continent at the speed of the Antarctic Circumpolar Current. This Antarctic Circumpolar Wave in sea surface temperature and sea sur-

face height also has an effect on the wind speed and wind stress curl distributions [*Jacobs and Mitchell*, 1996] which will have an effect on the rate of upwelling and the degree of surface mixing. *White et al.* [1998] have speculated that the Antarctic Circumpolar Wave results from sea surface temperature anomalies which form in the Western Pacific as part of El Niño and are communicated to the Southern Ocean by the western limb of the subtropical gyre circulation in the South Pacific. The observations of the frequency of variability in initial oxygen are consistent with that hypothesis.

[40] There are biogeochemical implications from an increase in the surface stratification in the Southern Ocean. Some Antarctic Intermediate Water, when subducted, crosses the Antarctic Circumpolar Current and travels
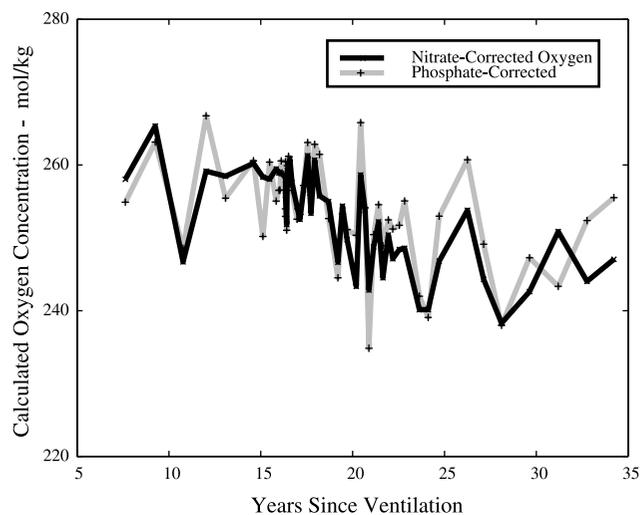

Figure 12. Variability in initial oxygen concentration in Antarctic Intermediate Water along 110°W, P18 plotted against ventilation age.

around the subtropical gyre, eventually feeding into the Equatorial Undercurrent through the Vitiaz Straits. According to some model results, the high-oxygen, high-nutrient Antarctic Intermediate Water input helps drive the equatorial biological pump as it is upwelled to the surface along the equator [*Toggweiler et al.*, 1991; *Toggweiler and Carson*, 1995]. Without this influx of oxygen and nutrients, it is possible that the extremely low oxygen conditions in the intermediate water of the Eastern Pacific basin could extend westward, increasing denitrification on the equator. Increasing the rate at which nitrate is lost to the atmosphere as nitrogen could make nitrate the limiting nutrient for primary production on the equator, thereby removing a natural impediment to the outgassing of CO_2 from waters warmed in the equatorial Pacific.

[41] This study has shown that the ratio of oxygen to nutrients can vary with time. Since Antarctic Intermediate Water provides a necessary component to the Pacific equatorial biological regime, this relatively high-nutrient, high-oxygen input to the Equatorial Undercurrent in the Western Pacific plays an important role in driving high rates of primary productivity on the equator, while limiting the extent of denitrifying bacteria in the eastern portion of the basin. Although the variability seen in Antarctic Intermediate Water today is not adequate to disrupt this balance, large-scale changes in the production of AAIW from the wind-driven circulation in the Antarctic Circumpolar Current might be able to shift the O_2 : P and O_2 : N relationship for intermediate waters in the South Pacific, increasing denitrification in the Eastern Pacific and eventually decreasing the bioavailable nutrients for the entire basin.

[42] Over longer timescales, like glacial to interglacial cycles, changes in the rate of denitrification in the Pacific Ocean could alter the degree to which the nutrients upwelled to the surface are used in primary production. In the Indian and Pacific Oceans, which are traditionally less well ventilated than the Atlantic Ocean because of their lack of a northern source of deep water, the limiting nutrient would become nitrate. If this were to occur, the rate at which deep waters from the Indian and Pacific were mixed with waters from the South Atlantic or ventilated in the Southern Ocean would determine the efficiency of the biological pump. Thus, changes in the wind-driven circulation in the Southern Ocean would become even more important to the global carbon and oxygen cycles.

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