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Chlorofluorocarbon evidence for rapid ventilation of the Ross Sea

S. E. TRUMBORE,*† S. S. JACOBS* and W. M. SMETHIE Jr*

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Abstract—Chlorofluorocarbon (CFC)-12 and -11 (CF_2Cl_2 and CFCI_3) measurements were made in seawater on the Ross Sea continental shelf and adjacent slope region in 1984. Concentrations of CFC-12 and CFC-11 in Ross Sea continental shelf water averaged nearly half that of saturated surface water. Circumpolar Deep Water within 50 km of the Ross Sea continental shelf also contained measureable CFC-12 and CFC-11, but an order of magnitude less than shelf waters. CFC-12 and CFC-11 concentrations in the deep water overlying the continental slope increased with depth, indicating recent ventilation and bottom water formation near the continental shelf.

Several water masses on the continental shelf that are commonly distinguished on the basis of temperature and salinity characteristics also varied in CFC content, and thus in their modes and rates of ventilation and renewal. A time-dependent model reproducing the 1984 sub-surface shelf water CFC concentrations demonstrates the relative importance of mixed layer entrainment, gas exchange through leads in the winter sea ice field, and mixing with source waters derived from the Circumpolar Deep Water. Model results show that mixed layer entrainment at the beginning of winter is the dominant process ventilating sub-surface shelf water in the eastern Ross Sea, while western shelf waters also require significant gas exchange during winter. Shelf water residence times can only be constrained by the model and available data to <10 years, but most probable values are ~2.5 years in the eastern Ross Sea and ~4 years in the western Ross Sea. CFC concentrations in water which has circulated beneath and has been modified by the Ross Ice Shelf indicate that the transformation time from High Salinity Shelf Water to Ice Shelf Water can be as short as 3.5 years. With reasonable oxygen consumption and nutrient regeneration rates, the balance of ventilation and mixing processes that reproduce observed shelf water CFC-12 concentrations also can account for observed oxygen and nitrate levels, if the western surface waters are undersaturated by ~10% at entrainment.

INTRODUCTION

CHLOROFLUOROCARBONS (CFC)-12 (CF_2Cl_2) and CFC-11 (CFCI_3) are anthropogenic, time-dependent tracers potentially useful in determining the processes and rates of deep water ventilation and bottom water formation in the Antarctic. CFC-12 and CFC-11 have been shown to be useful tracers of ocean mixing and ventilation on decadal time-scales (GAMMON *et al.*, 1982; BULLISTER and WEISS, 1983; WALLACE and MOORE, 1985; WEISS *et al.*, 1985; SMETHIE *et al.*, 1988; FINE *et al.*, 1988; WALLACE and LAZIER, 1988). Chlorofluorocarbons are chemically inert in seawater and have a well-established time history of input to the atmosphere based on release estimates (McCARTHY *et al.*, 1977; CHEMICAL

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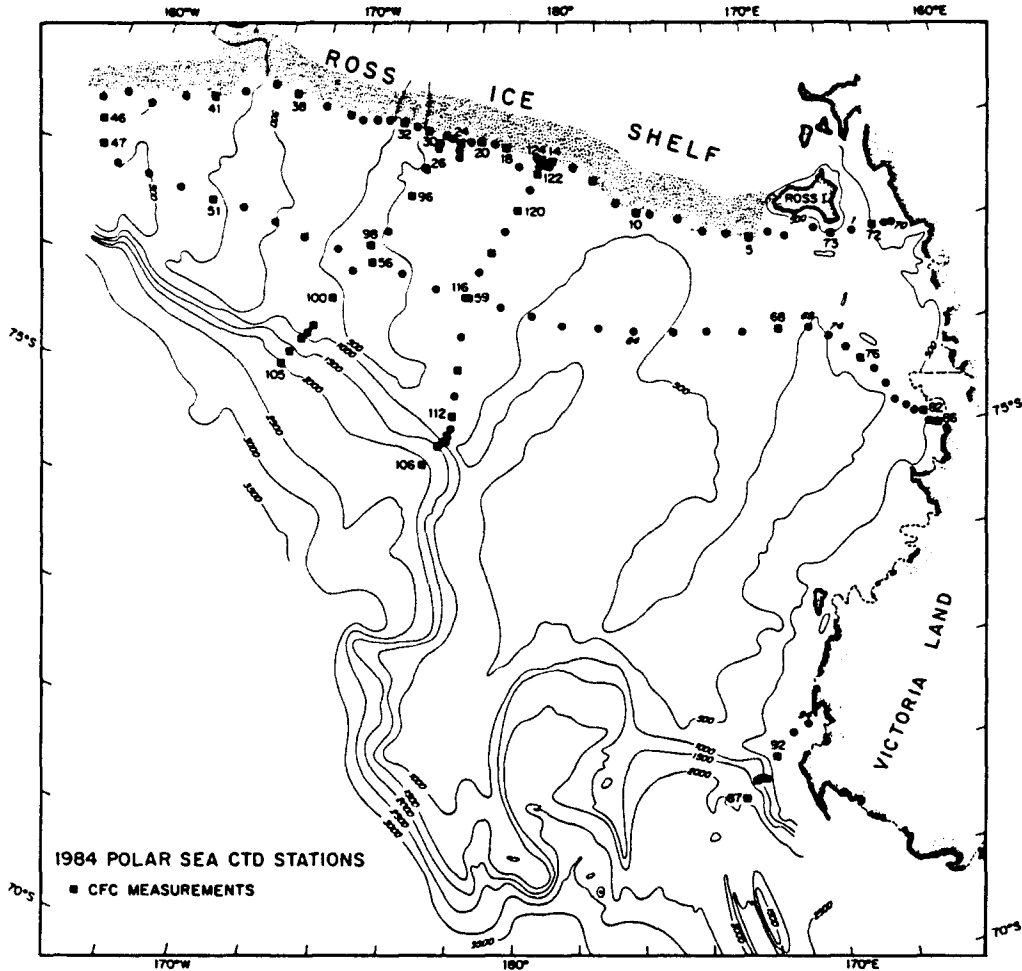


Fig. 1. Station location map for the *Polar Sea* 1984 expedition. Circles show CTD casts, boxes show CTD stations sampled for CFCs.

MANUFACTURERS' ASSOCIATION, 1980, 1983) and atmospheric measurements (e.g. CUNNOLD *et al.*, 1986). Because of their long (>50 year) tropospheric lifetimes (CUNNOLD *et al.*, 1983a,b, 1986), CFC-12 and CFC-11 are presently accumulating in the atmosphere. Although CFCs are well mixed within the northern and southern hemispheres, a gradient in the atmospheric mixing ratio for both CFCs is maintained between the hemispheres, reflecting the predominance of northern sources. CFC-12 and CFC-11 should prove especially valuable as tracers in the Southern Ocean, where the inputs and dynamic ranges of other time-dependent tracers such as ^3H and ^{90}Sr are small.

The CFC measurements reported here were made in the late austral summer (January–February) of 1984 aboard the U.S.C.G. *Polar Sea* (Fig. 1). In addition to CTD (conductivity–temperature–depth) profiles, water samples were collected on this cruise for analysis of CFC-12 and CFC-11, dissolved oxygen, nutrients, pCO_2 , total CO_2 and alkalinity. The purposes of measuring CFCs in the Ross Sea were to examine the time-

scales of ventilation and mixing for the various water types entering, residing on, and leaving the Ross Sea continental shelf, and to establish a baseline for comparison with future CFC measurements in this and surrounding areas. An understanding of the rates and processes controlling the evolution of Circumpolar Deep Water into shelf waters should be helpful to interpretations of chlorofluorocarbon measurements in Antarctic Bottom Water formed in the regions adjacent to the Antarctic continental shelf.

SAMPLING

Sampling and extraction methods for CFC analysis were adapted from those of BULLISTER (1984; reported in BULLISTER and WEISS, 1988). Water samples were collected from 5-l Niskin bottles equipped with plastic-coated stainless steel springs. Samples for CFC analysis were drawn into 100 ml ground glass syringes and stored in a seawater bath. Aliquots of 35 ml (measured in a calibrated volume loop) were transferred from the syringe to a stripping chamber, where they were bubbled with UHP nitrogen which had been purged of CFCs by passing through a Molecular Sieve 13X column. The CFCs were trapped out of the flow exiting the stripper onto a Porasil C column kept between -60 and -80°C . CFC-12 and CFC-11 driven off the subsequently isolated and heated (to 100°C) trap were analysed using shipboard electron capture gas chromatography. The GC used was a Shimadzu Mini-2 with an analytical column and a pre-column of Porasil C. The electron capture detector had a ^{63}Ni source and was operated at 285°C . N_2O coelution with CFC-12 was avoided by using a short column of Molecular Sieve 5a which retained N_2O but not CFC-12 at the column temperature of 75°C . This column, located between the analytical column and the detector, was valved out of the gas stream before CFC-11 entered it. The detector response to CFC-11 and CFC-12 was calibrated once or twice daily using a standard prepared from clean marine air. By this standard all reported concentrations are tied to the SIO 1984 scale (BULLISTER, 1984; WEISS et al., 1985).

Extremely high concentrations of CFC-11 in the lab van used for CFC analyses caused high system blanks for CFC-11 throughout the cruise. The high background levels resulted in contamination of some water samples during storage prior to analysis, and introduced problems with the reproducibility of CFC-11 in the standard gas. The lab air contained at least three orders of magnitude more CFC-11 than that present in clean marine air, but only approximately twice the atmospheric mixing ratio of CFC-12. Obviously contaminated samples (identified by anomalous CFC-11/CFC-12 ratios) were removed from the data set. The system blank levels, while usually undetectable for CFC-12, were consistently equivalent to a seawater concentration of 0.02 – 0.04 pmol l^{-1} (1 $\text{pmol} = 10^{-12}$ mol) for CFC-11. The average standard deviation between replicate water samples (both multiple syringes drawn from the same Niskin bottle and syringes drawn from Niskin bottles tripped at the same depth) was 0.02 pmol l^{-1} for CFC-12 and 0.04 pmol l^{-1} for CFC-11. These levels represent $<2\%$ of the concentrations measured in shelf waters and $<25\%$ of those in Circumpolar Deep Water. In addition, contamination of the sample loop used for standard gas calibrations resulted in relatively poor calibration of the detector response to CFC-11 through Sta. 95. Only CFC-12 profiles are shown here, although the CFC-11 distributions are very similar to those of CFC-12, and both are reported in Table 1. CFC-11 data for surface samples are not reported because concentration measurements in surface waters exceeded the range of our non-linear calibration curves, from which reliable surface extrapolations could not be obtained.

Table 1. Summary of temperature, salinity, nitrate, dissolved oxygen and chlorofluorocarbon (CFC) concentrations for selected February 1984 Ross Sea water samples processed for CFC. Water types were defined from T/S characteristics, resulting in subsets of size n from which average values were obtained. Equilibrated surface water dissolved gas concentrations were calculated from the solubility data of WARNER and WEISS (1985) for CFC-11 and CFC-12 and WEISS (1970) for dissolved oxygen. ND = not determined

Water mass	Temperature (°C)	Salinity	O ₂ (ml l ⁻¹)	NO ₃ ⁻ (µmol l ⁻¹)	CFC-12 (pmol l ⁻¹)	CFC-11 (pmol l ⁻¹)	CFC-11/CFC-12
Circumpolar Deep Water (CDW) (T > 1.0; S > 34.68; n = 12)	+1.17 ± 0.25	34.714 ± 0.016	4.39 ± 0.09	32.0 ± 0.1	0.10 ± 0.06	0.17 ± 0.17	1.7 ± 0.25
Warm Core (WMCO) (T > -1.1; S > 34.49; n = 12)	-0.97 ± 0.07	34.519 ± 0.019	5.94 ± 0.10	30.6 ± 0.3	1.02 ± 0.06	2.07 ± 0.14	2.03 ± 0.20
Deep Ice Shelf Water (DISW) (T < -2.0; S > 34.65; n = 8)	-2.11 ± 0.06	34.674 ± 0.012	6.49 ± 0.07	30.6 ± 0.6	1.03 ± 0.04	2.09 ± 0.12	2.03 ± 0.16
Low Salinity Shelf Water (LSSW) (-1.88 < T < -1.58; 34.48 < S < 34.58; n = 18)	-1.73 ± 0.16	34.538 ± 0.057	6.43 ± 0.17	30.2 ± 0.2	1.25 ± 0.10	2.58 ± 0.18	2.06 ± 0.28
High Salinity Shelf Water (HSSW) (-1.88 > T > -1.93; S > 34.81; P > 200; n = 22)	-1.91 ± 0.02	34.854 ± 0.027	6.71 ± 0.09	29.9 ± 0.6	1.60 ± 0.11	ND	ND
Measured Surface Water (n = 29)	-0.45 ± 0.60	34.14 ± 0.35	8.70 ± 0.68	16.8 ± 6.5	2.31 ± 0.19	ND	ND
Equilibrated Surface Water (ESW)	-1.0	34.3	8.3	—	2.30	5.55	2.40

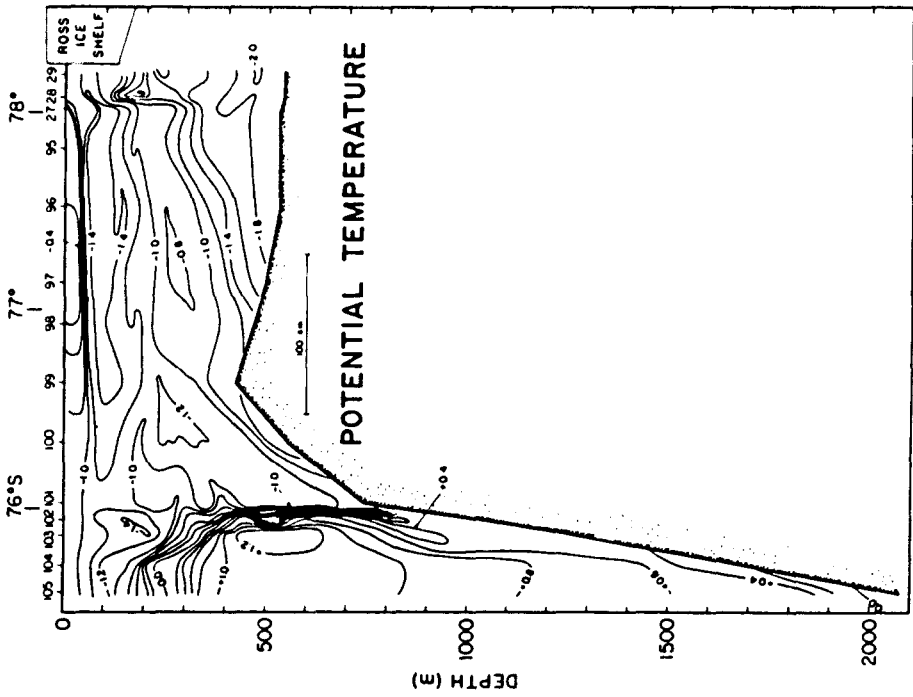
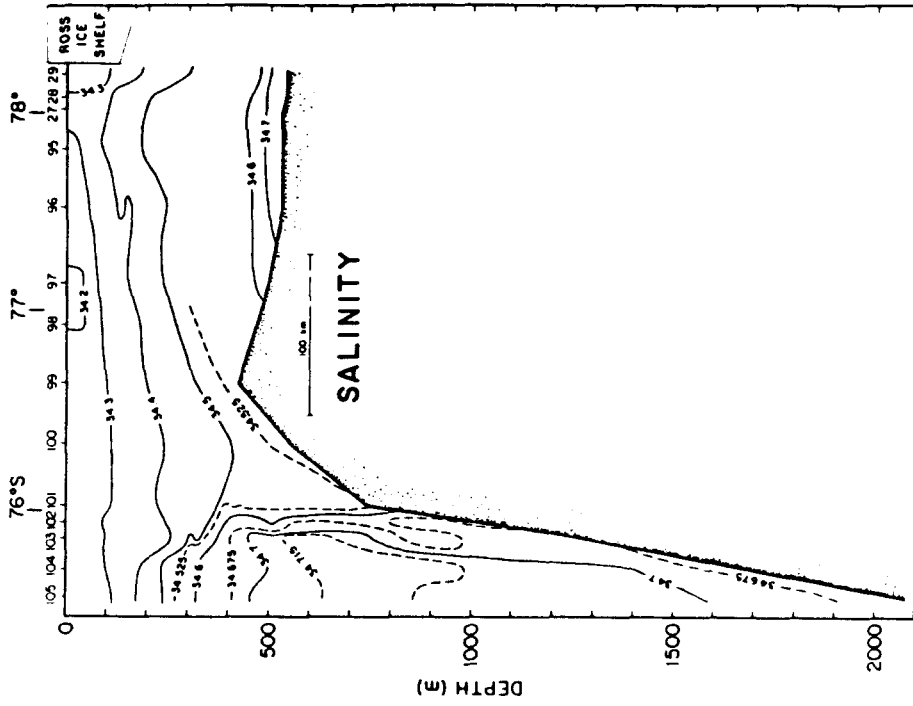
WATER MASS CHARACTERIZATION

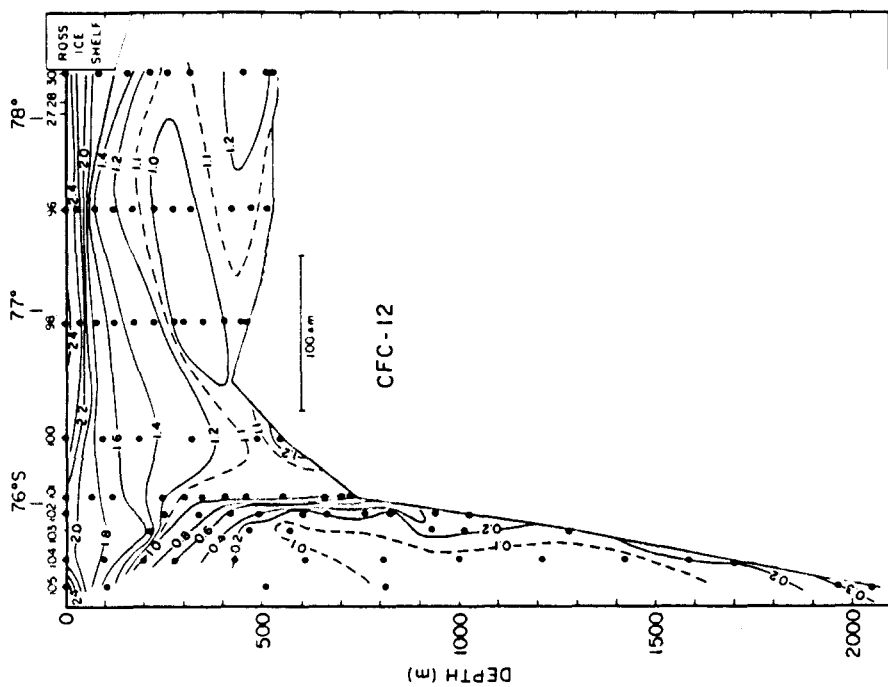
Circulation and hydrography in the vicinity of the Ross Sea continental shelf have been reviewed by JACOBS *et al.* (1985). The average potential temperature, salinity, dissolved CFC-12, CFC-11, O₂ and NO₃⁻ concentrations obtained on the *Polar Sea* 1984 cruise for the major water masses discussed below are given in Table 1. In some cases, the θ/S ranges of measurements selected to portray water mass types varies slightly from earlier criteria (JACOBS *et al.*, 1985) due to a different spatial distribution of stations or to regional or interannual changes in water mass characteristics. For example, the Table 1 range for Deep Ice Shelf Water (DISW) is restricted to temperatures colder than -2.0°C in order to identify core values, but the extent of that water over a wider shelf region can be seen in Fig. 6a where that limit is relaxed to $<-1.95^{\circ}\text{C}$. Water on the continental shelf is ultimately derived from Circumpolar Deep Water (CDW), which has upwelled over the continental slope north and east of the Ross Sea, and been modified by mixing with surface and slope waters. Subsequent interactions with the atmosphere, sea ice and glacial ice cool and alter the salinities of the shelf waters, which eventually move back into and under the CDW to ventilate the deep ocean. Whole or partial equilibration with atmospheric trace gases can occur through gas exchange and mixing with surface and other shelf waters. Direct gas exchange with the atmosphere is limited in winter to breaks in the sea ice canopy.

Transects of temperature and salinity (Fig. 2a,b) and CFC-12 concentration (Figs 2c, 3 and 4) that extend across the continental slope and shelf show a strong sub-surface front separating shelf and deep water over the upper continental slope. The deep source water (CDW) appears in Fig. 2 as a homogeneous water mass north of the continental shelf, with a temperature maximum exceeding 1.2°C and a salinity maximum above 34.715. The 1984 CFC-12 concentrations in this deep water ($<0.1 \text{ pmol l}^{-1}$ in Figs 2c and 3) were an order of magnitude less than in shelf water and 20 times less than in surface water. However, the presence of CFC at significantly greater than blank levels in CDW indicates that this progenitor water mass has interacted with slope waters at all levels within 50 km of the continental margin in the past 30 years. This is consistent with earlier hydrographic observations of lateral deep water modification near the Wilkes Land continental slope (CARMACK and KILLWORTH, 1978) and indicates that such processes also occur in and east of the Ross Sea.

Also evident in Figs 2–4 is an increase of CFC-12 from the mid-depth CDW minimum over the continental slope to the bottom. This incipient bottom water has been tagged with a recent atmospheric component obtained from the mixing of shelf waters with CDW near the continental shelf break. Our data are limited to depths of 2000 m, but show an increase in near-bottom CFC-12 with depth on the continental slope in the eastern Ross Sea (Figs 2c and 3). Even higher CFC-12 concentrations were measured between 1000 and 1500 m on the western slope (Fig. 4). Earlier hydrographic and current meter measurements have indicated that a westward drift near bottom along this continental slope (JACOBS *et al.*, 1970) continues west of 170°E (GORDON and TCHERNIA, 1972). These continental margin CFC sections thus substantiate a western Ross Sea source region for the high CFC concentrations reported near the base of the slope off Wilkes Land (MICHEL *et al.*, 1985).

At 300–500 m depths above the continental shelf in Fig. 2c, a layer of $<1.1 \text{ pmol l}^{-1}$ CFC-12 identifies an intrusion of relatively warm ($>-1^{\circ}\text{C}$) water from the continental slope region. This “warm” core (WMCO) persists year-round, and is associated with a





(c)

Fig. 2. Sections of (a) potential temperature (°C), (b) salinity (psu) and (c) CFC-12 (pM l⁻¹) from deep water across the continental shelf to the Ross Ice Shelf. The sub-surface slope front occurs between Stas 101 and 103.

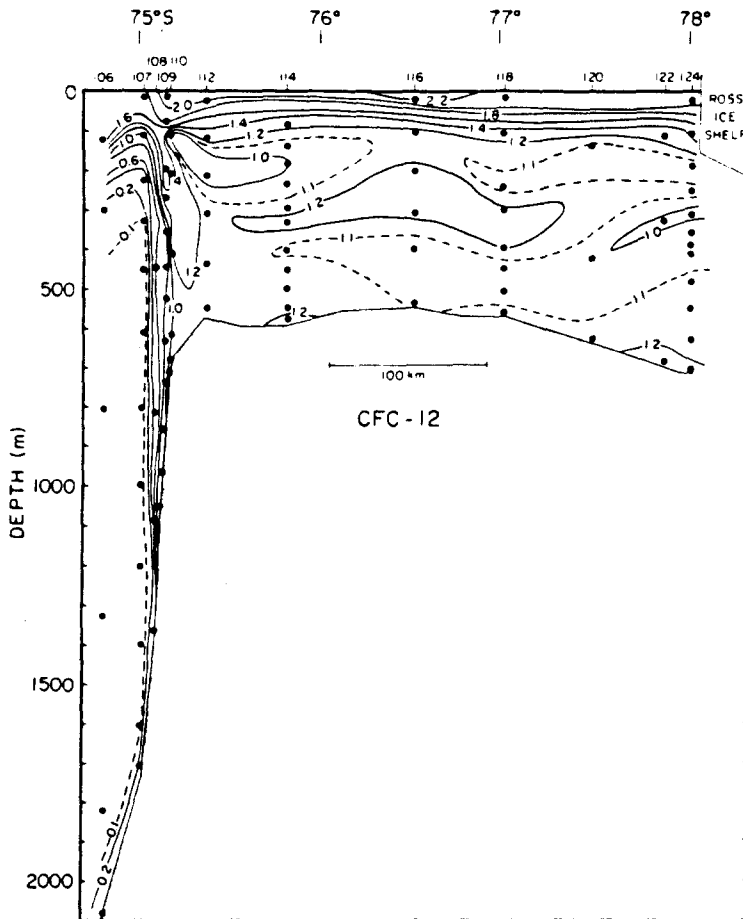


Fig. 3. Section of CFC-12 (pM l^{-1}) across the continental shelf through the Deep Ice Shelf Water, parallel to the section for WMCO in Fig. 2.

strong north-south flow into and out of the cavity under the Ross Ice Shelf (JACOBS *et al.*, 1985; PILLSBURY and JACOBS, 1985; KEYS *et al.*, 1990). The θ/S characteristics of this inflow and its CFC-12 content are consistent with a mixture of approximately 40% surface water and 60% CDW. This water may be drawn from the deep ocean pycnocline (GILL, 1973), or result from mixing near the slope front (JACOBS, submitted).

Another mid-depth CFC minimum (Fig. 3) crosses the continental shelf and slope 100–200 km west of the section depicted in Fig. 2. This CFC minimum is associated with coldest water on the shelf, the Deep Ice Shelf Water (DISW) of JACOBS *et al.* (1985). The DISW has been cooled to below the surface seawater freezing point by melting and other interactions at the base of the Ross Ice Shelf. Ice Shelf Water also has been observed near ice shelves in the Weddell Sea and elsewhere, and is believed to play a role in bottom water formation (e.g. JACOBS *et al.*, 1970; WEISS *et al.*, 1979; FOLDVIK and GAMMELSRØD, 1988; JACOBS *et al.*, 1985; SCHLOSSER *et al.*, 1990).

East-west sections of CFC-12 adjacent to the ice shelf front and across the mid-shelf region are shown in Figs 5 and 6c. Although CFC sampling along these transects was sparse

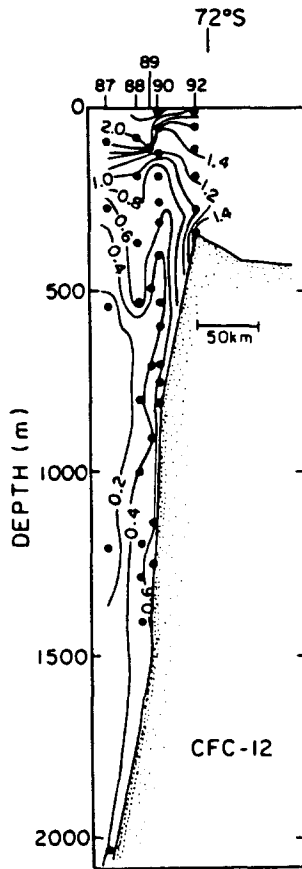


Fig. 4. Section of CFC-12 (pM l^{-1}) across the continental shelf-slope break in the western portion of the Ross Sea.

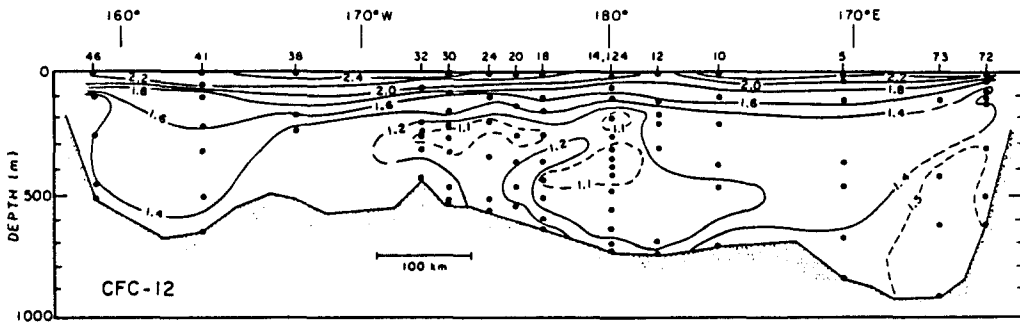
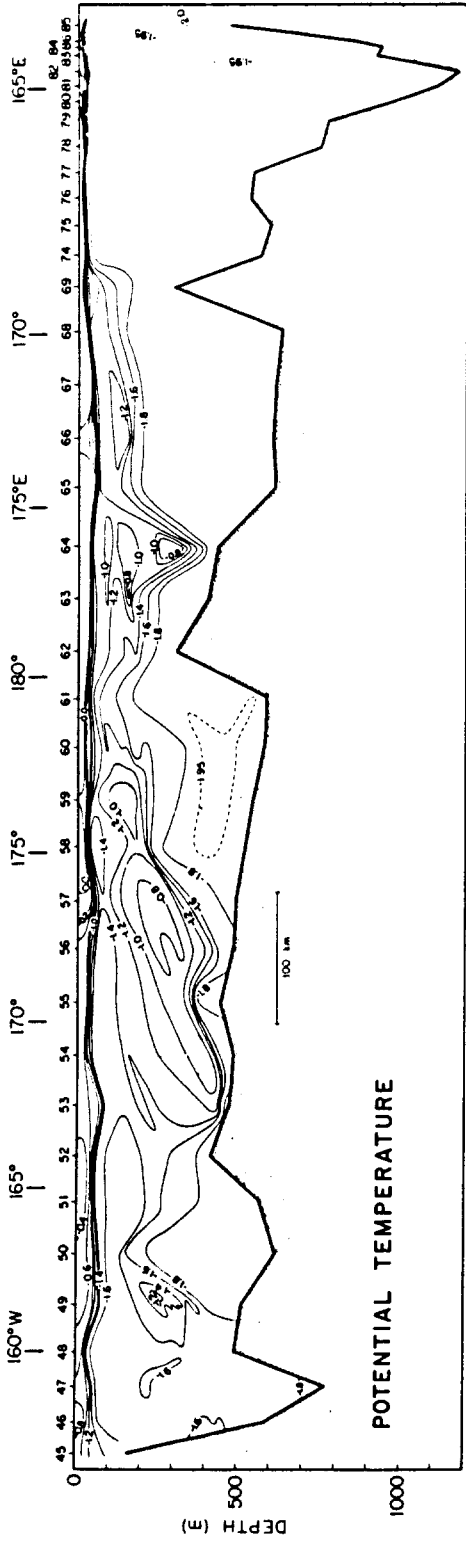
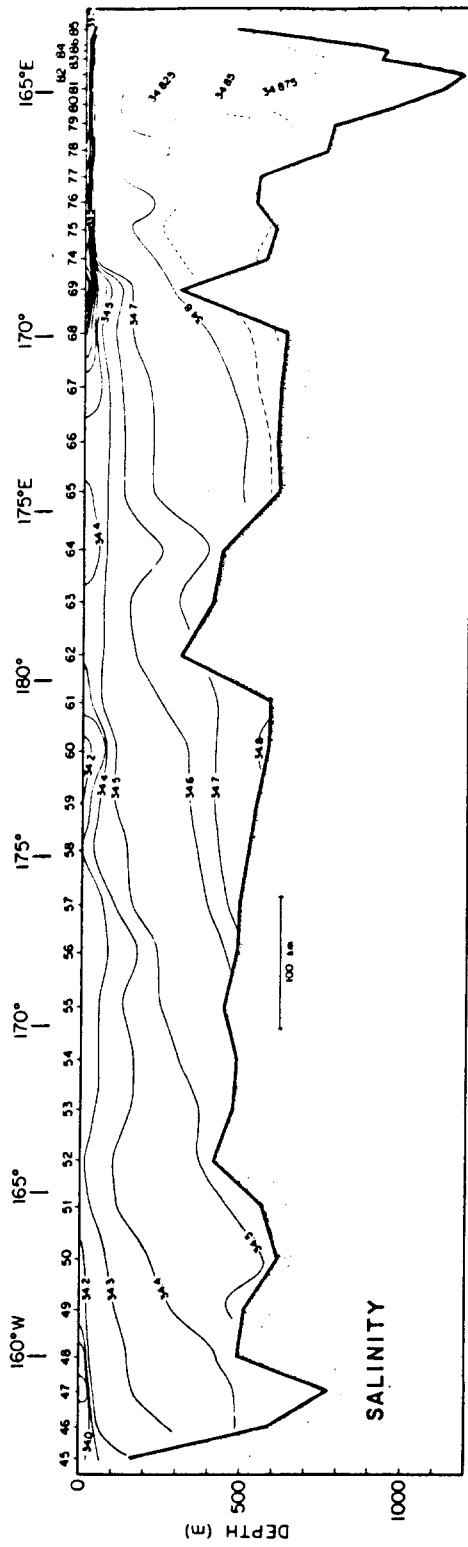


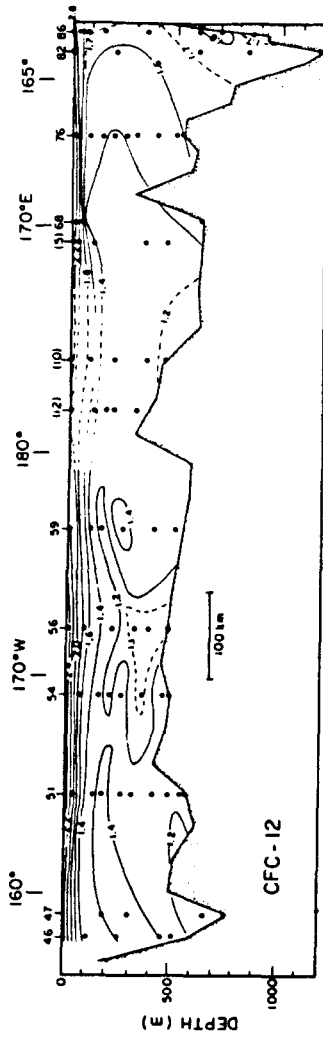
Fig. 5. East-west section of CFC-12 (pM l^{-1}) parallel and adjacent to the Ross Ice Shelf front.



(a)



(b)



(c)

Fig. 6. East-west sections of (a) potential temperature ($^{\circ}\text{C}$), (b) salinity (psu), and (c) CFC-12 (pM l^{-1}) across the central continental shelf. Note that stations in parentheses in (c) have been taken from the more southerly transect (Fig. 5). Isopycnals, parallel isohalines, and high and low salinity shelf waters (HSSW and LSSW) are roughly divided by the 34.7 isohaline. The primary "warm" intrusion (WICO) from north of the continental shelf is the $> -1^{\circ}\text{C}$ region between 168°W and 177°W . The Deep Ice Shelf Water (DISW) appears on this section as the $< -1.95^{\circ}\text{C}$ region between 175°W and 180°W .

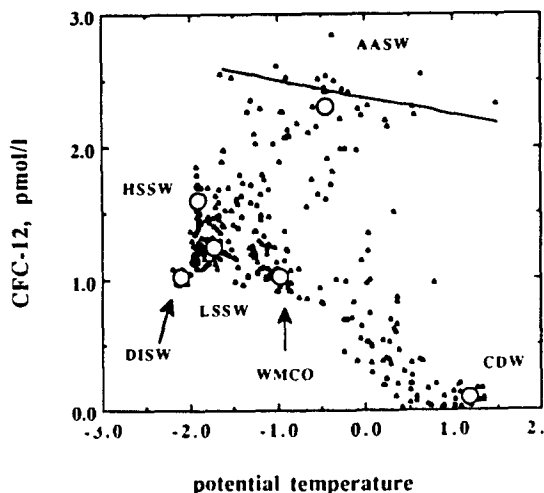


Fig. 7. CFC-12 vs potential temperature for all 1984 data. The line showing decreasing CFC-12 with increasing temperature is the expected relation for surface water equilibrated with 346.4 ppt CFC-12 in the atmosphere (WARNER and WEISS, 1985). Water mass averages (Table 1) appear as open circles, and are defined in the text and Fig. 8 caption.

(see Fig. 6, caption) the principal water masses can easily be identified. High Salinity Shelf Water (HSSW; $S > 34.75$) on the western portion of the continental shelf and Low Salinity Shelf Water (LSSW; $S < 34.6$) on the eastern side comprise the major portion of sub-surface water on the continental shelf. These two reservoirs, relatively homogeneous in their different CFC contents, are isopycnally separated by the tongues of WMCO water ($\theta > -1.0^{\circ}\text{C}$) and DISW ($\theta < -1.95^{\circ}\text{C}$) that extend across the central portion of the shelf. Ice Shelf Water also appears at the western end of Fig. 6a, in association with local floating glaciers and a western boundary current that originates beneath the ice shelf. Spatial and temporal variability is highest in the central sector, as evidenced by the different minima on nearby Stas 56 and 98, or 59 and 116 (Figs 2, 3 and 6). HSSW contains more dissolved chlorofluorocarbon and oxygen than does LSSW (Table 1), reflecting different processes or rates of ventilation and renewal for these shelf waters. CFC-12 increases with depth in the western Ross Sea, consistent with the hypotheses that ventilation of this water mass is driven by intense ice formation, brine release and vertical convection in winter coastal polynyas (JACOBS *et al.*, 1985).

Figures 7 and 8 illustrate the relationship of CFC-12 to potential temperature and salinity. The surface water CFC-12 concentrations observed during the 1984 Polar Sea cruise were close to, but averaged slightly below, the saturation level. Variations above and below the surface equilibration line are likely to be caused by local wind-induced vertical mixing, recent removal and melting of the sea ice cover, and rapid surface heating. WARNER (1988) observed undersaturation in surface water for both CFCs, especially at polar latitudes. In this regard, it is of interest to compare the surface water average and distribution in our Fig. 7 with Fig. 9 in KEIR *et al.* (submitted). Although taken a year later over the Wilkes Land continental margin ($\sim 150^{\circ}\text{E}$), the Keir *et al.* surface CFC-12 values are limited to $\sim 2.1 \text{ pM kg}^{-1}$. This may be due to the more persistent sea ice cover along that coastline relative to the Ross Sea. Water mass averages identified in Figs 7 and 8,

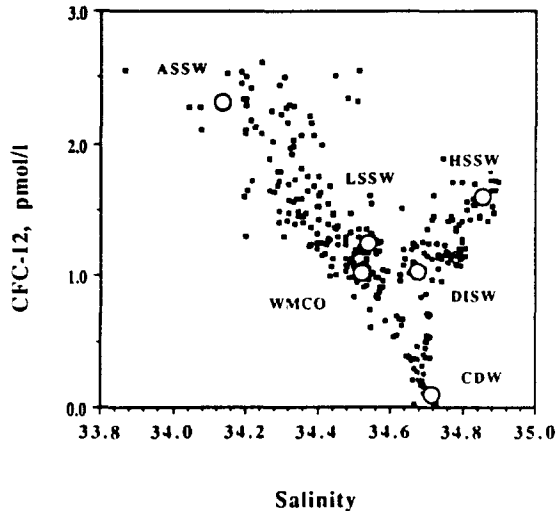


Fig. 8. CFC-12 vs salinity for all 1984 data. (See Fig. 7 caption) AASW = Antarctic Surface Water, CDW = Circumpolar Deep Water, DISW = Deep Ice Shelf Water, HSSW = High Salinity Shelf Water, LSSW = Low Salinity Shelf Water, WMCO = Warm Core. The AASW average is pulled toward lower salinities by several very low values in the western Ross Sea.

calculated from subsets of the data differentiated by T/S properties, do not represent all of the observed modes. For example, a cluster of points in Figs 7 and 8 has mean characteristics of -1.94°C , 34.757 psu and 1.17 pmol l^{-1} in temperature, salinity and CFC-12. This Ice Shelf Water variant is found in the central Ross Sea and near the ice shelf front, but deeper and at a higher temperature, salinity and CFC concentration than the DISW extrema.

Dissolved oxygen (O_2) is compared with potential temperature in Fig. 9. Surface water O_2 in the austral summer is often supersaturated by up to 15%. Surface undersaturation is observed in association with upwelling water at the slope front. The upper 25 m in the western Ross Sea directly overlies HSSW and is characterized by low nutrient and high O_2 concentrations, evidence of the late-summer phytoplankton bloom in that region (NELSON and SMITH, 1986). Dissolved oxygen and temperature are linearly correlated in most sub-surface waters ($\text{O}_2 < 7 \text{ ml l}^{-1}$), indicating that mixing processes are rapid enough to dominate gradients which would be formed by O_2 consumption in the sediments or sub-surface shelf waters.

CFC-11/12 RATIO

Since the rate of increase of CFC-11 in the atmosphere has been greater than that of CFC-12, the ratio of CFC-11/CFC-12 has changed with time (Fig. 10; derived in the next section) and sometimes can be used to determine the time since atmospheric contact for a particular water mass. The regulation of CFC use in spray cans in the U.S. during the late 1970s decreased the rate of CFC-11 increase, and the 11/12 ratio in the atmosphere has remained essentially constant since about 1975. Equilibrated surface water with temperatures below 0°C and 34.3 psu salinity should have had a ratio of 2.3–2.4 for 1984 and the 10 previous years (Fig. 10). BULLISTER (1989) has reported CFC-11/12 ratios of about 2.2 in

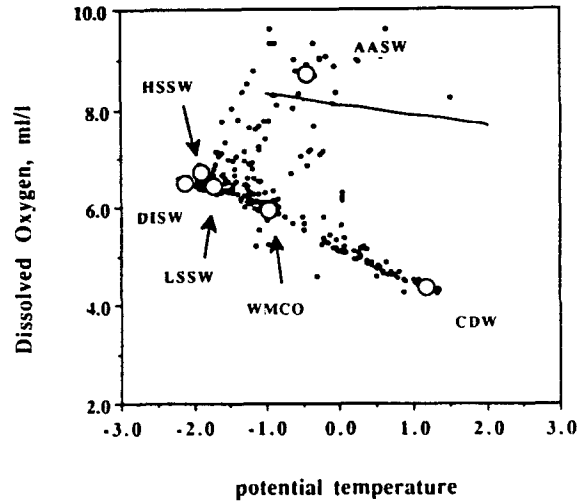


Fig. 9. Dissolved oxygen (ml l^{-1}) vs potential temperature for all 1984 data. (See Fig. 7 caption.)

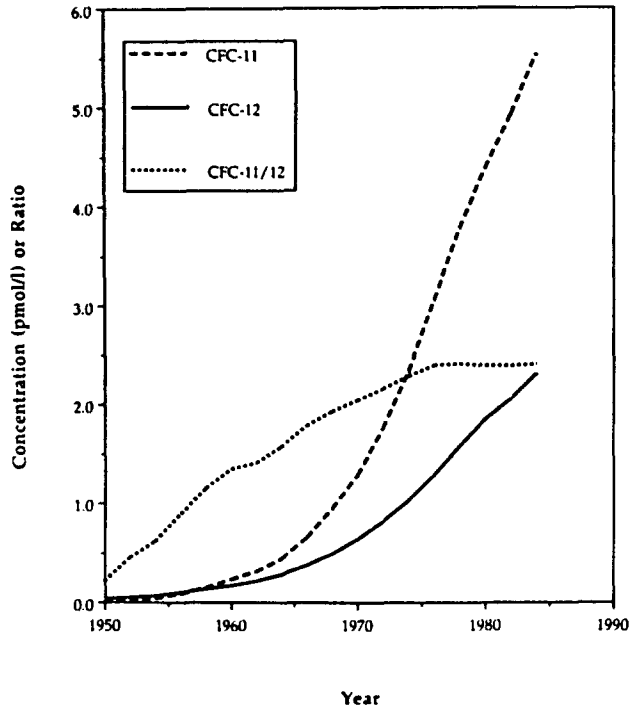


Fig. 10. Time histories of CFC-12 and CFC-11 through 1984 for surface water with a temperature and salinity of -1.0 and 34.3 calculated from the atmospheric time history and WARNER and WEISS' (1985) solubility data.

near-surface waters of the Weddell Sea in early 1987. We are not reporting CFC-11 data for surface waters, but average CFC-11/12 ratios for sub-surface shelf waters were consistently between 2.0 and 2.1 in 1984. Similar ratios were obtained in 1985 surface and shelf waters along the Wilkes Land coast (KEIR *et al.*, submitted). CFC-11/12 ratios of 2.0–2.1 would have been observed in equilibrated surface waters in 1969–1971. However, the 1984 CFC-12 concentrations in sub-surface waters exceed the 1969–1971 equilibrium concentration, and other renewal estimates indicate that ventilation of shelf waters has occurred since that time (JACOBS *et al.*, 1985). Low CFC-11/12 ratios observed in undersaturated surface waters (WARNER, 1988) may be due to slower air–sea equilibration of CFC-11. If equilibrated surface water at 0°C is rapidly cooled to the freezing point ($\sim -1.9^\circ\text{C}$), CFC-12 and CFC-11 will become undersaturated by 10 and 12%, respectively (WARNER and WEISS, 1985). If CFC-12 subsequently achieved equilibrium with the atmosphere, but CFC-11 did not before mixing down into sub-surface waters, the resulting ratio would be 2.04. The transition from open water to nearly complete sea ice cover takes place from late February through early April on the Ross Sea continental shelf (JACOBS and COMISO, 1989), in some regions within the span of several days, but we have no observations of the CFC or O_2 saturation levels in surface water during the preceding cooling period. Additional information in the rates and processes of shelf water ventilation can be derived from modeling of the CFC concentrations.

MODEL

The distribution of CFC on and near the Ross Sea continental shelf is consistent with our previous understanding of the water mass interactions developed from temperature, salinity and ^{18}O data (JACOBS *et al.*, 1985). Three processes can contribute to the ventilation of water on the Ross Sea continental shelf: autumn entrainment of the summer surface mixed layer, direct gas exchange with the atmosphere through polynyas and leads in the winter sea ice, and mixing between different water masses. The water column is stratified during summer, as melting ice and insolation create a low density surface layer. This surface layer attains approximate equilibrium with CFC in the atmosphere, but is mixed down into the sub-surface shelf waters when it cools and becomes more saline with the formation of sea ice at the end of summer. Although most of the continental shelf is ice-covered during winter, gas exchange through polynyas and leads in the sea ice field allows additional CFC to be pumped directly into the poorly stratified shelf waters. Mixing with water derived from north of the continental shelf also alters the shelf water CFC concentrations. Since LSSW and HSSW contained more CFC than the WMCO and DISW in 1984 (Fig. 8), mixing with those intrusions would tend to counter the increases in CFC resulting from mixed layer entrainment and gas exchange.

The relative importance of summer mixed layer entrainment, gas exchange during winter, and mixing with CFC-depleted source waters in ventilating sub-surface shelf waters can be determined through modeling the shelf water CFC concentrations. A time-dependent box model that simulates the time history of CFC-11 and CFC-12 in the shelf, surface and source waters is illustrated schematically in Fig. 11. The time step in the model is one month, to accommodate the seasonal nature of ventilation processes. The three processes are parameterized in the model as follows:

(1) Entrainment of summer mixed layer. Once a year (in April), a mixed layer, representing some portion of the total water depth, is mixed down into the water column.

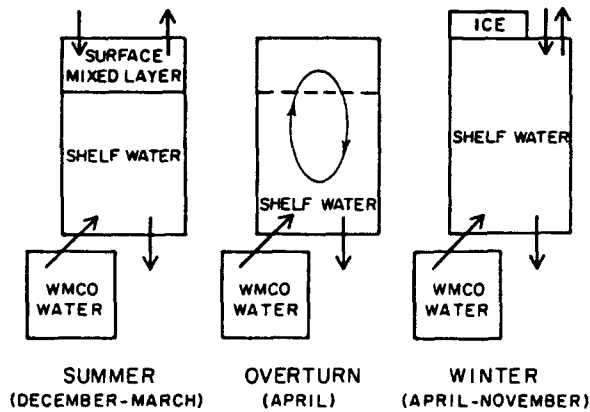


Fig. 11. Schematic illustration of the seasonal model described in the text, showing the processes of mixed layer entrainment, gas exchange and mixing with source water.

This step accounts for gas exchange that has occurred during the austral summer. The homogenized concentration after entrainment is expressed as:

$$C_d(t) = \frac{h_m C_{esw}(t) + h_d C_d(t-1)}{h_m + h_d},$$

where t is the time step of the model (one month), C_d is the shelf water concentration, C_{esw} is the concentration of equilibrated surface water, calculated from the atmospheric time history and the solubility data of WARNER and WEISS (1985), and h_m and h_d are the thicknesses of the mixed layer and the shelf water below the mixed layer, respectively. The mixed layer thicknesses for HSSW and LSSW, based on 1984 CTD profiles, are initially taken as 25 and 40 m, and the total water depths ($h_d + h_m$) average 600 and 450 m, respectively (JACOBS *et al.*, 1989). It should be emphasized that summer mixed layers on the continental shelf are quite variable in form and thickness and our station coverage was neither spatially uniform nor at the beginning of autumn. The ≈ 25 m surface layer we encountered in the western Ross Sea in February 1984 (Fig. 6) may have been thinner than average summer mixed layers overlying the HSSW (JACOBS *et al.*, 1970), and greater thicknesses are common near the ice shelf front.

(2) Gas exchange. Gas exchange through polynyas and leads between ice floes is assumed to occur during the 8-month period from April (following entrainment of the mixed layer) through November (beginning of summer mixed layer formation). The increase in concentration of CFCs due to gas exchange is:

$$\frac{dC_d(t)}{dt} = \frac{kf[C_{esw}(t) - C_d(t-1)]}{h_m + h_d},$$

where f is the fraction of ice free surface area, and $h_m + h_d$ is the water depth. Gas exchange is assumed to affect the entire homogenized water column. The gas exchange coefficient, k , is estimated from an empirical formula relating it to wind speeds between 2 and 18 m s^{-1} (WANNINKHOF, personal communication, 1990):

$$k = 0.18 u^2 \sqrt{\frac{600}{Sc}},$$

where Sc is the Schmidt number for CFC-12 and CFC-11 at 0°C, and u is the wind speed in m s^{-1} at 10 m height above sea level. This closely approximates the relationship between gas exchange and wind speed reported by LISS and MERLIVAT (1986), for $u = 3.6\text{--}13 \text{ m s}^{-1}$. Molecular diffusivities for CFC-11 and CFC-12 at 0°C used to calculate the Schmidt numbers were estimated using the relation from WILKE and CHANG (1955). The Schmidt numbers for CFC-12, CFC-11 and O_2 used in the model were 3354, 3649 and 1800, respectively. Gas exchange was calculated in the model using two parameters, the wind speed (estimated from local weather stations; SAVAGE *et al.*, 1985), and the fraction of winter sea surface that is free of ice. Both surface winds and sea ice cover are temporally and spatially variable, but the average ice cover over the entire continental shelf stays within a few per cent of 86% throughout the winter (Fig. 3 in JACOBS and COMISO, 1989). The coastal area in the western Ross Sea overlying the HSSW experiences higher wind speeds during the winter months and has more open water than the eastern LSSW region.

(3) Mixing with older source waters. Exchange with WMCO water (parameterized as a mixture of 40% surface and 60% Circumpolar Deep Water) is assumed to occur year-round, at a constant rate (r):

$$\frac{dC_d}{dt} = \frac{r}{V_d} [(0.4)C_{esw} + (0.6)C_{cdw} - C_d],$$

where C_{cdw} is the concentration of CFC in CDW, and V_d is the volume of shelf water. In 1984, C_{cdw} was only 1% of surface water concentrations, so C_{cdw} is assumed to be zero throughout the modeling exercise. Since processes (1) and (2) involve no import or export of water from the shelf, the rate of mixing with the WMCO is a measure of sub-surface shelf water residence time. It should be noted that WMCO water is unlikely to be the only source for shelf water renewal. The deep temperature minimum near the slope front and the slope and shelf water east of the Ross Sea could evolve into LSSW during the winter (JACOBS *et al.*, 1985). In addition, this model focuses upon the open shelf region, which also receives an external component in the form of DISW from beneath the Ross Ice Shelf. Because of similar CFC-12 concentrations, the lower-temperature DISW could substitute for some portion of the WMCO renewal, bringing in higher salinities and more dissolved oxygen.

The concentrations of CFC-12 and CFC-11 in the atmosphere for the three decades prior to our measurements were derived as in SMETHIE *et al.* (1988) from published estimates of release rates (CHEMICAL MANUFACTURERS' ASSOCIATION, 1980, 1983) and assuming tropospheric lifetimes of 111 years for CFC-12 and 74 years for CFC-11 (CUNNOLD *et al.*, 1986). The atmospheric burden of CFC was converted to a mixing ratio by normalizing to observed CFC-11 and CFC-12 at Cape Mears, Oregon in 1976. This normalization factor was applied to all previous years. To account for the inter-hemispheric mixing time, the reconstructed northern hemisphere record was lagged by 18 months, based on the comparison of Atmospheric Lifetime Experiment stations in the northern (Cape Mears, Oregon) and southern (Cape Grim, Tasmania) hemispheres (CUNNOLD *et al.*, 1983a and b, 1986). Southern hemisphere CFC mixing ratios for the years 1976–1984 were obtained from observations reported by RASMUSSEN and KHALIL (1983, 1986) at the South Pole. This record was converted to the SIO 1984 scale using the factors

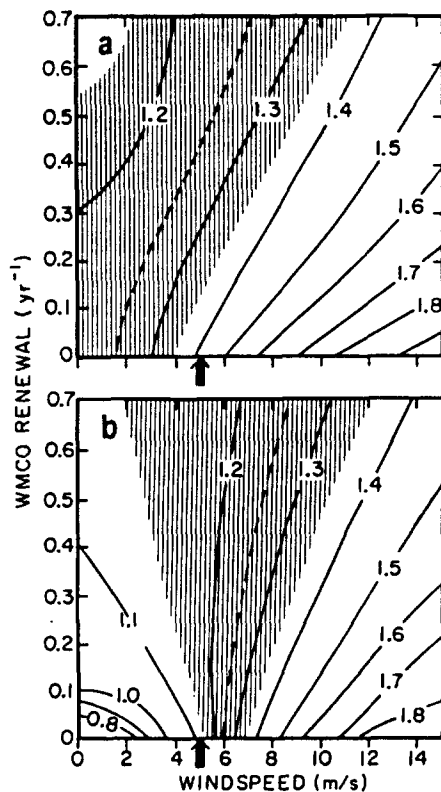


Fig. 12. Results of the time-dependent model for CFC-12 in Low Salinity Shelf Water (see text for description of the model), for two different mixed layer thicknesses. CFC-12 concentrations calculated for January 1984 are plotted as a function of average wind speed (April–November; *x*-axis) and the rate of renewal by WMCO source water (*y*-axis). CFC-12 values are contoured, and a shaded area brackets the concentration of CFC-12 observed in LSSW, $1.25 \pm 0.10 \text{ pmol l}^{-1}$. The sensitivity of the model results to changes in the mixed layer thickness can be seen by comparing (a) (mixed layer = 40 m) and (b) (mixed layer = 20 m). The fraction of ice-free surface area was assumed to be 0.15 for both (a) and (b). An arrow shows estimated wind speed from observations near the Ross Ice Shelf front (approximately 5 m s^{-1} ; SAVAGE *et al.*, 1985).

given in RASMUSSEN and KHALIL (1986) and BULLISTER (1984). The atmospheric mixing ratios (in dry air) of CFC-12 and CFC-11 measured during the cruise ($346.4 \pm 2.6 \text{ pptv}$ CFC-12 and $194.7 \pm 6.3 \text{ pptv}$ CFC-11) agreed with concentrations measured by RASMUSSEN and KHALIL (1986) and ELKINS *et al.* (1988) at the South Pole during the same period. The CFC solubilities used to convert atmospheric mixing ratios to saturated surface water concentrations were those reported by WARNER and WEISS (1985), assuming a surface water temperature of -1.0°C and a salinity of 34.3 psu.

The model was used to determine the relative importance of the three processes (mixed layer entrainment, winter gas exchange, and mixing with source water) in determining the observed 1984 CFC concentrations in Low and High Salinity Shelf Waters. The model results are displayed in Figs 12a,b for LSSW and 13a,b for HSSW. Each figure shows the variation in calculated 1984 CFC-12 concentration with wind speed (*x*-axis) and WMCO

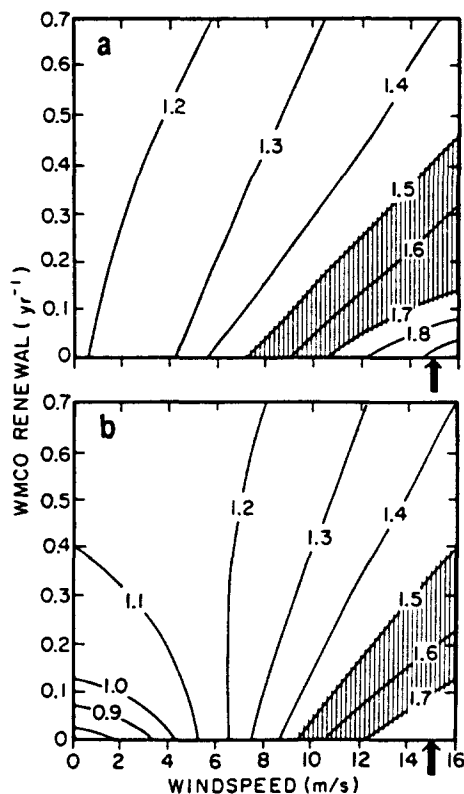


Fig. 13. Results of the time-dependent model for CFC-12 in High Salinity Shelf Water, plotted as in Fig. 12. (a) uses a mixed layer depth of 50 m, and (b), 25 m. The fraction of ice-free surface area was assumed to be 0.15 for both (a) and (b). An arrow shows approximate wind speed measured near the Terra Nova Bay Polynya (SAVAGE *et al.*, 1985).

water renewal rates (r/V_d ; y-axis) for a given summer mixed layer thickness and fraction of ice-free winter surface area. The plots are contoured with CFC-12 isopleths, and the shaded regions show the suite of wind speeds and WMCO water exchange rates which bracket the observed 1984 LSSW and HSSW CFC-12 concentrations (1.25 ± 0.10 and 1.60 ± 0.11 pmol l^{-1} , respectively). To show the sensitivity of the model to mixed layer entrainment, the wind-speed exchange rate relations are shown for two mixed layer thicknesses for each water mass. Not shown are variations in the fraction of ice-free area, assumed to equal a shelf-wide average of 15% throughout the winter. A one-third increase in this parameter (from 15 to 20%) would be equivalent to a decrease in the model wind speed of $1\text{--}2$ m s^{-1} . The surface winds over the Ross Sea are estimated from scattered coastal stations, and are probably no more accurate than the sea ice cover derived from satellite microwave measurements.

Although both CFC-12 and CFC-11 were modeled, only the CFC-12 results will be discussed here. The predicted CFC 1984 11/12 ratios were always 2.3–2.4, higher than the observed values (Table 1). The model of KEIR *et al.* (submitted) for shelf water formation adjacent to Wilkes Land near 150°E also yielded higher ratios than were observed.

Disequilibrium in surface waters at the time of entrainment appears to be the most likely explanation for discrepancies in 11/12 ratios between our model and the observations.

DISCUSSION

Low Salinity Shelf Water (LSSW)

Entrainment of 40 m summer mixed layer into LSSW, with no additional input from winter gas exchange, predicts a 1984 CFC-12 concentration of 1.1–1.2 pmol l⁻¹, close to the 1984 observed value of 1.25 ± 0.10 pmol l⁻¹ (Table 1, Fig. 12a). Additional CFC input by winter gas exchange must be balanced by mixing with the CFC-depleted WMCO. Figure 12a and b shows the relation between renewal rate and wind speed for mixed layer thicknesses of 40 m (Fig. 12a) and 20 m (Fig. 12b), assuming a 15% ice-free area during the winter months. Because of the small difference in CFC content between LSSW and WMCO, the model is not very sensitive to changes in the WMCO mixing rate. The average mixed layer thickness is probably closer to 40 m (Fig. 12a), and wind speed can be estimated at approximately 5 m s⁻¹ from April through November (SAVAGE *et al.*, 1985). This constrains the time-scale for renewal to less than 10 years, with a most probable value of 2.5 years at the intersection of 5 m s⁻¹ and 1.25 pmol l⁻¹.

High Salinity Shelf Water (HSSW)

The entrainment of a summer mixed layer with a thickness of 25 or 50 m, assuming no input from gas exchange or mixing with the WMCO, results in 1984 HSSW concentrations of <1.2 pmol l⁻¹ for CFC-12 (Fig. 13a,b). Since the observed CFC-12 concentration in 1984 HSSW was 1.60 pmol l⁻¹, which would require a mixed layer thickness of 100 m, gas exchange during winter must play a significant role in the ventilation of this water mass. This is reflected by the high wind speeds required to produce the 1984 HSSW CFC-12 concentration (>7 m s⁻¹ in Fig. 13a). With a wind speed in the western Ross Sea of 15 m s⁻¹ (SAVAGE *et al.*, 1985) and a 15% ice-free surface area in winter, the renewal time with respect to mixing with a WMCO source is constrained to 2.4–10 years (Fig. 13). Most of the ventilation of HSSW probably occurs via coastal polynyas like the one in Terra Nova Bay (near Sta. 86 in Fig. 1), where sustained high winds have been measured. Somewhat lower wind speeds and a greater percentage of ice-free surface are likely to be more appropriate to the entire western Ross Sea (HSSW) area, but the most probable renewal rates are 4–5 years, corresponding to 1.6 pmol l⁻¹ and 15 m s⁻¹. This renewal time would lengthen by about half if the replacement were 50% WMCO and 50% DISW, rather than 100% WMCO.

Collectively, Figs 12 and 13 demonstrate that the ventilation processes occurring on the Ross Sea continental shelf differ with location. Mixed layer entrainment appears sufficient to ventilate the LSSW, with gas exchange roughly balancing mixing with the WMCO. A combination of summer mixed layer entrainment and winter gas exchange is required to provide the higher degree of ventilation observed in HSSW. The rate of renewal by mixing with the WMCO also appears to be slower in the western Ross Sea. Using values for the model input parameters that most closely approximate the observed mixed layer thicknesses of 25 and 40 m, average wind speeds of 5 and 15 m s⁻¹, a winter average ice-free surface area of 15%, and the 0.1 pmol l⁻¹ standard deviation of CFC measurements (Table

1). then shelf water renewal rates can only be limited to <10 years. However, the water mass average CFC concentrations and these realistic values of the model input parameters indicate shelf water renewal rates of less than 5 years with respect to exchange with the WMCO. These rates are similar to a previous estimate of ~6 years (JACOBS *et al.*, 1985), derived from ice and salt budget constraints.

Areal differences in ventilation processes become important when considering the inputs of other gases, such as CO₂, to Antarctic shelf waters. The time required for equilibration of CO₂ with surface waters is several times longer than for gases like O₂ and CFCs (BROECKER *et al.*, 1980). The input of CO₂ to HSSW and LSSW should thus be primarily through mixed layer entrainment and remineralization of organic matter rather than by gas exchange.

Deep Ice Shelf Water (DISW)

DISW is derived from HSSW, and a residence or transformation time beneath the Ross Ice Shelf can be calculated from the HSSW and DISW CFC-12 concentrations and the time history of CFC-12 in the HSSW. Two ways of doing this are with a time-dependent one-box model and a stream tube model. For both methods it is assumed that water beneath the ice shelf is completely isolated from contact with the atmosphere.

The time-dependent one-box model yields a residence time. It is assumed that HSSW flows into a well mixed reservoir beneath the Ross Ice Shelf and that DISW flows out of this box. The CFC-12 concentrations in DISW, C_{DISW} , is given by

$$\frac{dC_{\text{DISW}}}{dt} = \frac{1}{\tau} (C_{\text{DISW}} - C_{\text{HSSW}}),$$

where t is time, C_{HSSW} is the CFC-12 concentration in HSSW and τ is the residence time. This equation is solved numerically using the output of the HSSW model for C_{HSSW} and varying τ until the model C_{DISW} matches the observed concentrations. With the mean CFC-12 concentrations observed in HSSW and DISW in 1984 (Table 1) a residence time of 7 years is obtained. The volume of water beneath the ice shelf that participates in the HSSW/DISW evolution may be taken as $118 \times 10^3 \text{ km}^3$ from Fig. 1 in GREISCHAR and BENTLEY (1980), considering only the area >100 km south of the ice front. The DISW ($\theta < -1.95^\circ\text{C}$) emerges from beneath the shelf ice over an area of about 50 km^2 where the CFC-12 is $<1.1 \text{ pmol l}^{-1}$, near 180° in Fig. 5. With this volume and cross-sectional area, the 7 year residence time is equivalent to a mean outflow velocity of 1.1 cm s^{-1} , close to the measured average over a 7-month period at that location (PILLSBURY and JACOBS, 1985). However, the assumption that the water beneath the Ross Ice Shelf is well mixed is not supported by temperature and salinity observations there (JACOBS, *et al.*, 1979, 1985).

A stream tube model (MACAYEAL, 1985), based on the assumption that HSSW is transformed in DISW as it flows beneath the ice shelf and mixes little with surrounding water, is probably more realistic than the box model. The CFC-12 concentration in DISW is then assumed to have been the concentration in HSSW when it entered the region beneath the ice shelf. The effect of basal melting on dilution of the CFC content is <1% and can be neglected. The year of inflow is determined from the CFC-12 time history in HSSW and the transit time is the difference between 1984 and that year. Using the CFC-12 values in Table 1 and Fig. 10, a transit time of 5.5 years is obtained. However, the values in

Table 1 are averages from stations throughout the Ross Sea continental shelf. The HSSW and DISW CFC-12 concentrations on stations closest to the ice shelf front average 1.44 and 1.12 pmol l^{-1} , which yield a transit time of 3.5 years. If the HSSW/DISW plume makes a 1000 km round trip beneath the ice shelf (twice the distance from the ice front to the grounding line where the glacial ice begins to float), that would correspond to an average velocity of 0.9 cm s^{-1} .

An outflow of 1 cm s^{-1} over 50 km^2 would correspond to a DISW production rate of $0.5 \times 10^6 \text{ m}^3 \text{ s}^{-1}$ (0.5 Sv), similar to the $0.4\text{--}1.0 \text{ Sv}$ production rates calculated for the Weddell Sea (FOLDVIK *et al.*, 1985; HELLMER and OLBERS, 1989). From the 1984 salinity data, the dilution between inflowing HSSW and outflowing DISW is 0.18 psu (Table 1), equivalent to the addition of $79 \text{ km}^3 \text{ y}^{-1}$ meltwater over that portion of the ice shelf base that interacts with the main plume. The 0.2°C temperature decrease between HSSW and DISW would only provide sufficient heat to melt half that volume of ice, suggesting ice crystal formation in the water column or shelf water salinities that were lower at the time of inflow 3.5–5.5 years earlier. If single-station profiles are representative of the HSSW, then salinities may have been significantly lower in 1982, but differed little in 1978 (Fig. 4.1 in JACOBS, 1985). Repeated time-dependent tracer measurements should allow refined calculations of the ocean's role in the basal mass balance.

From 1977–1978 bomb-derived ^{14}C data, MICHEL *et al.* (1979) estimated an exchange rate between the sub-ice shelf cavity and open Ross Sea of less than 6 years. Their data may apply to a shallower, lower-density circulation cell, although some observations were made more than 400 km south of the ice front. The low residence and transit times for water beneath the ice shelf are also supported by direct current measurements (PILLSBURY and JACOBS, 1985; JACOBS, submitted), which include sustained drifts of several cm s^{-1} in and out of the sub-ice shelf cavity. It seems unlikely that this region, which can experience relatively little wind-driven and thermohaline forcing, has a more active circulation than the open Ross Sea. This supports the idea that the shelf water renewal times are closer to the values derived from the CFC averages than to the <10 year constraint that results from the standard deviation of those averages.

Dissolved oxygen (O_2) and nitrate (NO_3^-)

The steady state concentration of dissolved O_2 in shelf waters, like the transient CFC concentration, is determined by the rates of mixed layer entrainment, gas exchange and mixing with source water. In addition, O_2 is produced and consumed by biological processes which do not alter CFC content. A minimum O_2 consumption rate of $0.03\text{--}0.06 \text{ ml l}^{-1} \text{ y}^{-1}$ for shelf waters can be derived from the decrease in O_2 during the 3.5 to 7-year evolution of HSSW into DISW (Table 1) under the Ross Ice Shelf. We used the most probable combination of model parameters reproducing 1984 CFC-12 concentrations in LSSW and HSSW to estimate the O_2 depletion rate in the shelf waters, which can occur both in the water column and underlying sediments. The soundness of these estimates is checked by modeling dissolved NO_3^- , which is also affected by processes involving mixing and biological activity, but not gas exchange. O_2 consumption rates were converted stoichiometrically to regenerate NO_3^- from oxidation of organic matter with a C/N ratio of 105/15 ($\Delta\text{NO}_3^-/\Delta\text{O}_2 \approx -9$). Limitations on the use of O_2 and NO_3^- in the model are their variability in surface waters and the lack of observations there at the time of entrainment.

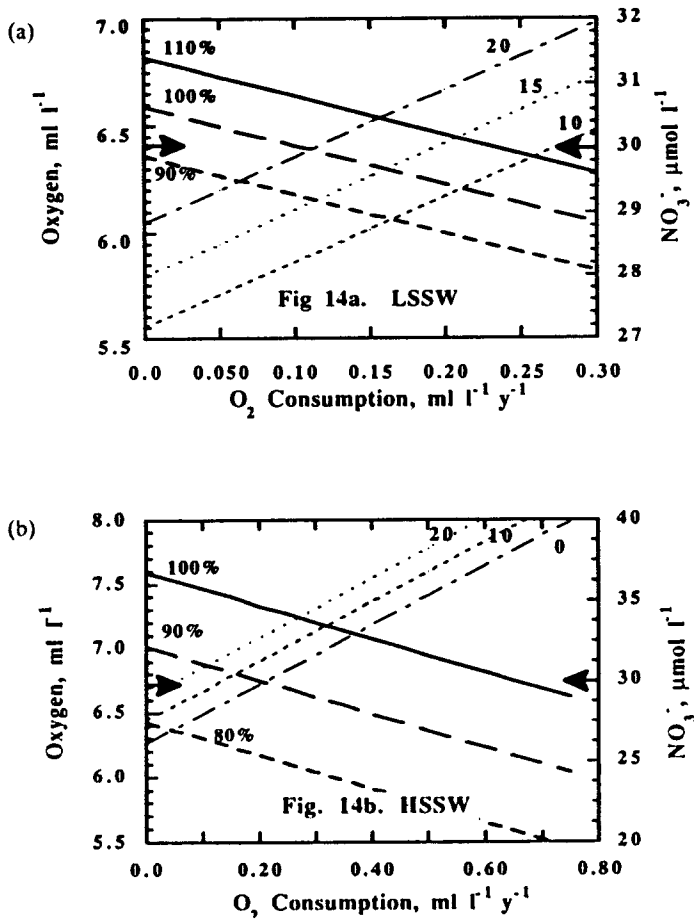


Fig. 14. Modeled concentrations of O₂ and NO₃⁻ as a function of O₂ consumption/NO₃⁻ regeneration in LSSW (a) and HSSW (b), for different O₂ and nutrient levels in the surface layer that is entrained at the end of summer. In each case, model parameters were used that best reproduced the 1984 CFC-12 concentrations in LSSW and HSSW (Figs 12 and 13), with O₂/NO₃⁻ set at -9. The average observed LSSW and HSSW O₂ and NO₃⁻ concentrations are designated by arrows.

Variations in O₂ and NO₃⁻ concentrations predicted by the model for different O₂ consumption rates are shown in Fig. 14a,b as a function of O₂ and nitrate levels in the surface layer that is entrained at the end of summer. The model parameters for LSSW and HSSW mixed layer entrainment, wind speed and residence time with respect to WMCO renewal were 40 and 25 m, 5 and 15 m s⁻¹, and 2.5 and 4.5 years, respectively. Winter ice-free surface area was assumed to be 15% in both cases.

The distribution of dissolved O₂ and NO₃⁻ in LSSW can be reproduced with O₂ utilization rates of 0.11–0.25 ml l⁻¹ y⁻¹ (Fig. 14a). This exceeds the rate measured in temperate continental shelf sediments (0.06 ml l⁻¹ y⁻¹, when extrapolated to a 600 m water column; CHRISTENSEN *et al.*, 1987), but is lower than a rate calculated for the Sargasso Sea thermocline (0.5 ml l⁻¹ y⁻¹; JENKINS, 1980). A similar O₂ consumption rate, ~0.06–0.2 ml l⁻¹ y⁻¹, yields the observed concentrations of both O₂ and NO₃⁻ in HSSW.

However, this combination of model parameters requires that the surface layer entrained in the fall be undersaturated by about 10% (Fig. 14b), which may be unrealistic. Rapid cooling of surface water from 0 to -1.9°C will produce water $\sim 5\%$ undersaturated in O_2 . Primary productivity is seasonally high in surface waters overlying HSSW on the Ross Sea continental shelf (NELSON and SMITH, 1986), and the sediments in that sector can contain more than 2% organic carbon (DUNBAR, 1988). Thus there is fuel for oxygen consumption. Although the oxidation of sedimentary organic matter could produce a significant lowering of O_2 concentration with water depth, vertical O_2 gradients are minimal in the HSSW, probably due to rapid vertical mixing in an isothermal water column that is near the surface freezing temperature.

In summary, the model simulates the oxygen and nitrate concentrations using the most probable parameter values obtained from fitting the CFC-12 measurements. However, these biologically-mediated parameters cannot provide additional constraints without a better understanding of the mixed layer evolution during the fall season. Observations of transient tracers with inputs or *in situ* behavior significantly different from CFC-11 and CFC-12 would be beneficial. Possible candidates include tritium, with its input spike in the early 1960s, CFC-113 which has been increasing more rapidly in the atmosphere than CFC-11 and CFC-12 during the past decade, and Kr-85. The latter has an input history similar to CFC-11 and CFC-12, but decays with a half-life of 10.8 years after leaving the sea surface. KEIR *et al.* (submitted) have used CFC, radiocarbon and tritium data to calculate shelf water renewal times of ~ 8 years in 600-m deep basins on the Antarctic continental shelf near 150°E .

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