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## Biogeochemical regimes, net community production and carbon export in the Ross Sea, Antarctica

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### Abstract

The net community production (NCP) of the Ross Sea, from the early austral spring (mid-October) to the austral summer (mid-February), has been estimated from the seasonal drawdown of CO<sub>2</sub> concentrations integrated over the top 100 m of the water column. The deficits in nutrients and CO<sub>2</sub> indicate three distinct biogeochemical regimes. The regime in the southwestern Ross Sea (Region I) had relatively shallow mixed layers and was dominated by diatom growth, as evidenced by a silicate (Def(Si)) to NCP removal ratio ( $0.11 \pm 0.04$ ) that was similar to the silicate-to-carbon ratio found in diatoms growing in temperate regions. High NCP values ( $4.9\text{--}8.7 \text{ mol m}^{-2}$ ) and low ratios of surplus total organic carbon (Surp(TOC)) to NCP (from 0.27 to 0.67) show high organic carbon export out of the upper 100 m of the water column. The second regime (Region II), located in the center of the southern Ross Sea polynya, also had high NCP's ( $4.4\text{--}10.8 \text{ mol m}^{-2}$ ) but the mixed layers were deeper. The average Def(Si)/NCP ratio was  $0.04 \pm 0.02$ , much lower than the southwestern sector and consistent with the observed growth of the haptophyte *Phaeocystis antarctica*. An increase in Def(Si) and the Def(Si)/NCP ratio during re-occupations of selected stations indicate the presence and persistence of diatom growth late into the summer. The third regime (Region III), in the northeastern Ross Sea, had shallow mixed layers and a wider range of Def(Si)/NCP ratios (0.10–0.31), indicating variations in silicate-to-carbon uptake by diatoms. The low NCP's

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(1.2–4.2 mol C m<sup>-2</sup>) that distinguished this area also may be due to micro-nutrient deficiencies in addition to prolonged ice coverage. NCP over the continental shelf of the Ross Sea (441,000 km<sup>2</sup>, defined by the 1000-m isopleth) is estimated to be  $25 \pm 10$  Tg of carbon per year, with a mean rate of  $4.8 \pm 1.9$  mol m<sup>-2</sup> yr. By mid-February, the productivity peak of the 1997 growing season had passed, and  $19 \pm 7\%$  of NCP remained in the upper 100 m as DOC, which presumably would not be exported but remineralized prior to the next growing season. During the same time period,  $16 \pm 25\%$  of NCP had already been removed from the upper 100 m as sinking biogenic particles, leaving 65% present in the POC fraction to be exported later or remineralized. High export of organic carbon (> 50% of NCP) was shown in both diatom- and *Phaeocystis*-dominated regimes. © 2000 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Past studies of primary productivity in the Ross Sea and other parts of the Southern Ocean have found high variability of phytoplankton production in location and time of onset and senescence (Priddle et al., 1986; Poisson et al., 1993; Smith et al., 1996). For the purposes of constructing a regional estimate of biological production that is representative of the whole growing season, many investigators have chosen to look at the net community productivity (NCP). Theoretically, NCP is a measure of the net production of autotrophs (phytoplankton production) minus the respiration of the entire community (Eppley, 1989). Practically, NCP is calculated as the deficit of CO<sub>2</sub> in the upper water column resulting from an imbalance between photosynthesis and respiration in a time period bracketed by measurements. Many estimates of NCP have been made by quantifying the seasonal depletion of nutrients (e.g. Jennings et al., 1984; Nelson et al., 1996; Bates et al., 1998). In these studies, nutrient depletion was converted to carbon removal by employing a C/N or C/P ratio based on Redfield et al. (1963) or other studies (e.g., Copin-Montegut and Copin-Montegut, 1978). Still other estimates of NCP have been made with direct measurements of TCO<sub>2</sub>, pH and pCO<sub>2</sub> to correct for alkalinity changes and gas exchange (Codispoti et al., 1982, 1986; Bates et al., 1998). In each case, an assumption must be made that the amount of nutrients or carbon transported into or out of the study area during the growing season was small. The effects of sea–air gas exchange, CaCO<sub>3</sub> precipitation or dissolution, and dilution or condensation as a result of melting or ice freezing also can change the carbon budget in ways unrelated to photosynthesis and respiration. In order to monitor changes in the elemental ratios of nutrient and carbon uptake, we make deficit calculations using TCO<sub>2</sub>, pCO<sub>2</sub> and a multi-nutrient inventory. In addition to estimating NCP in the Ross Sea, this study uses measurements of particulate organic carbon (POC) and dissolved organic carbon (DOC) to predict the fraction of NCP exported out of the upper 100 m of the water column. Under the assumption that all NCP is converted to organic carbon, it can then be inferred that the fraction of NCP that has been exported can be estimated from the difference between the NCP and surplus total organic carbon (where TOC = DOC + POC) remaining at the surface. Using a second assumption that all POC will eventually sink

out of the surface, a potential export can be estimated from the fraction of NCP remaining as surplus POC at the surface.

The results of this study parallel those of Nelson et al. (1996), which show that the bloom in the Ross Sea can be divided into three different biogeochemical regimes that have been observed throughout the Antarctic. The regimes we observed were characterized by different dominant species, such as the diatom-dominated ice edge bloom region, the *Phaeocystis*-dominated region, and the low-productivity and diatom-dominated shelf break and open-ocean region. An understanding of the differences in these biogeochemical regimes and their associated physical environments will lead to useful predictions of biological responses to changes in the physical environment such as those predicted to accompany global warming.

## 2. Methods for measurements

### 2.1. Study areas

Stations were occupied aboard the RVIB *Nathaniel B. Palmer* in the Ross Sea as part of the US Joint Global Ocean Flux Study (JGOFS) Antarctic Environment Southern Ocean Process Study (AESOPS) from October 15 to November 6, 1996 (early spring) and from January 13 to February 9, 1997 (summer). Both cruises sampled transects along 76°30'S latitude between 165°E and 176°W (Fig. 1). The summer cruise also included a visit to 74°S where hydrographic measurements were completed on and off the continental shelf. Additional hydrographic measurements were made in two locations at the edge of the Ross Ice Shelf and one site in near-shore fast ice. Several locations along 76°30'S latitude and one location along the Ross Ice Shelf were re-occupied with a week interval between each occupation.

Following Nelson et al. (1996), the Ross Sea study area was divided into three regions, which were bounded by the land to the west and south and the 1000-m isopleth to the east and north (Fig. 1). Cape Adare defines the northwestern extent of the Ross Sea in this study and Cape Colbeck the southeastern limit. Region I was considered the near-shore area, extending east to the 170°E meridian from the western shoreline and north to 74.5°S from the Ross Ice Shelf. Region II was defined to the west by the 170°E meridian, to the east by the 180°E meridian, to the south by the Ross Ice shelf, and to the north by 74.5°S. An east-reaching limb of Region II was extended about 120 km off the Ross Ice shelf to Cape Colbeck on the basis of the observations made at stations 9, 23 and 24 (Fig. 1b) and underway pCO<sub>2</sub> data (Fig. 2). Region III was bounded to the east by the continental shelf break (represented by a dotted line in Fig. 1), to the west by the shoreline, and to the south by Regions I and II.

### 2.2. Analytical methods

All calculations in this study are based on data from hydrocasts obtained nine stations during the early spring cruise (November 1996) and 28 stations during the

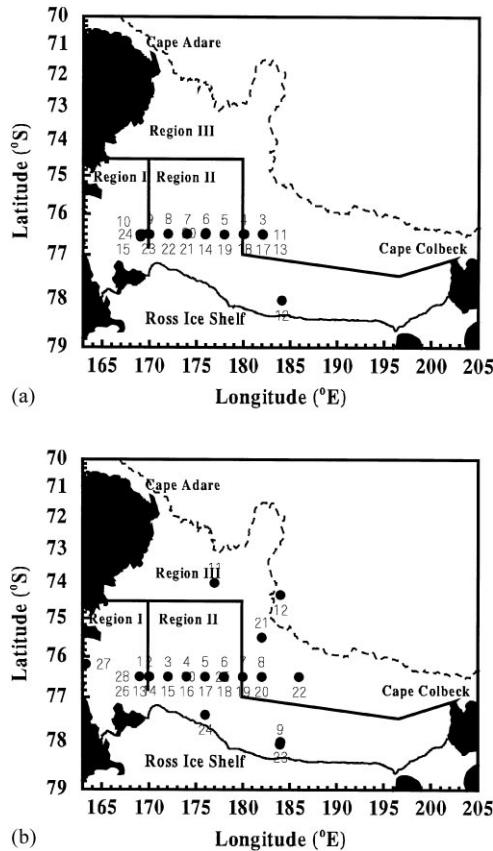


Fig. 1. Station locations. (a) Early spring cruise from October 15, 1996 to November 6, 1998. (b) Summer cruise from January 13, 1997 to February 9, 1997. Solid lines are boundaries defining the approximate position of three biogeochemical regimes in the Ross Sea during the 1996–97 growing season. The fine zonal line in the south shows the boundary of the Ross Ice Shelf. The dashed line shows the 1000 m isopleth, which approximates the location of the shelf break.

summer cruise (January 1997). Salinity normalization schemes and comparison of deep-water values were made using the data from an autumn cruise (March 1997) and an austral spring cruise the following year (November 1997).

### 2.3. Organic carbon

Twenty-milliliter samples for dissolved organic carbon (DOC) were collected in acid-cleaned and pre-combusted 40-ml vials sealed with Teflon-lined caps. Sampling for DOC took place after  $\text{TCO}_2$  and  $\text{pCO}_2$  samples had been taken at the rosette. Analysis was performed using a high-temperature combustion (HTC) method (Hansell et al., 1997; Carlson et al., 1998). The precision of the measurement has been estimated to be  $1.0 \mu\text{M}$ .

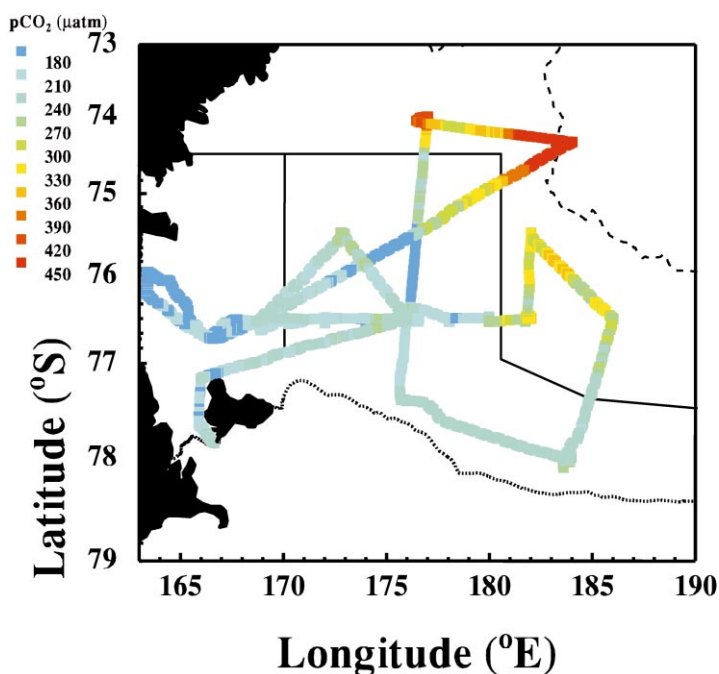


Fig. 2. Surface  $p\text{CO}_2$  during the summer cruise January 23 to February 2, 1997.  $p\text{CO}_2$  values have been calculated for a constant temperature of  $4^\circ\text{C}$  (Chipman et al., 1993). Solid lines are boundaries defining the approximate position of three biogeochemical regimes in the Ross Sea during the 1996–97 growing season. The fine zonal line in the south shows the boundary of the Ross Ice Shelf. The dashed line shows the 1000 m isopleth, which approximates the location of the shelf break.

Particulate organic carbon (POC) samples were collected in 2.0-l polypropylene bottles. One liter of sample was filtered through a pre-combusted Whatman GF/F glass-fiber filter under a low vacuum and stored at  $-20^\circ\text{C}$ . The storage, acidification and final analysis with a Carlo-Erba Model 252 elemental analyzer was done according to JGOFS protocol (<http://usjgofs.who.edu/protocol.html>). Because many of the POC samples were taken from different hydrocasts than the  $\text{TCO}_2$  and DOC samples, each POC sample was normalized by salinity and total inorganic nitrogen (TIN) drawdown to account for any mesoscale variability between casts at a single station.

#### 2.4. Inorganic carbon

During the early spring cruise  $\text{TCO}_2$  was determined by coulometry using a single operator multiparameter metabolic analyzer (SOMMA) system (Johnson et al., 1985, 1987, 1993) with an estimated precision of  $\pm 1.4 \mu\text{mol kg}^{-1}$ . This system was standardized using calibrated volumes of UHP  $\text{CO}_2$  gas at a precisely measured temperature and pressure. In addition to  $\text{TCO}_2$ , pH and alkalinity also were measured. pH was measured spectroscopically using methods of Clayton and Byrne (1993) with

a precision of 0.001. Alkalinity was measured using methods of Millero et al. (1993) with a precision of  $\pm 2 \mu\text{eq kg}^{-1}$ . During the summer and following spring,  $\text{TCO}_2$  was measured using a LDEO coulometer system (Chipman et al., 1993) with an estimated precision of  $\pm 1.3 \mu\text{mol kg}^{-1}$ , which also was standardized using calibrated volumes of 99.998%  $\text{CO}_2$ . Total  $\text{CO}_2$  measurements from all cruises were corrected with routine measurements of manometrically determined certified reference material (CRM) (<http://www-mpl.ucsd.edu/people/adickson/> - Batch # 31, # 32, # 33, # 34, # 35; Dickson, 1990). The  $\text{pCO}_2$  was measured during the summer cruise using a gas chromatograph (Chipman et al., 1993) with a precision better than  $\pm 0.25\%$  ( $\sim \pm 1 \mu\text{atm}$ ). All  $\text{CO}_2$  samples were treated with 200  $\mu\text{l}$  of 50% saturated  $\text{HgCl}_2$  and stored at  $4^\circ\text{C}$  until analysis not more than 24 h after being collected.

Surface-ocean  $\text{pCO}_{2(\text{sw})}$  and atmospheric  $\text{pCO}_{2(\text{atm})}$  were calculated from samples taken underway using an infrared analyzer (Licor 6252). Atmospheric samples were dried and pumped directly to the analyzer for measurement. Seawater  $\text{pCO}_2$  was measured using a continuous stream of water equilibrated with a carrier gas in a 30-l shower-type equilibrator (Takahashi et al., 1997). Air equilibrated with water sample was dried and the  $\text{CO}_2$  concentration (mole fraction- ppm) determined every 3 min. The underway  $\text{pCO}_2$  measurements were standardized using five  $\text{CO}_2$ -air reference gas mixtures calibrated against the World Meteorological Organization (WMO) standards (Scripps Institute of Oceanography, unpublished data, 1994). The partial pressure determined for the atmospheric and equilibrated water samples was computed from the dry gas concentration and ambient barometric pressure (Atmospheric Instruments Research Inc. Model AB-2A) and corrected for water vapor pressure by assuming saturation at seawater temperatures. The sea-air  $\text{pCO}_2$  difference,  $\Delta\text{pCO}_2$ , was calculated at each station location throughout the course of the cruise. In addition to  $\text{pCO}_2$  measurements made during the summer and early spring cruises, several other cruises in this area during the same year allowed us to estimate seasonal changes of  $\Delta\text{pCO}_2$  through the bloom season at each station. The calculated  $\Delta\text{pCO}_2$  for each station over the time of the bloom was then fit to a sine function using a linear least-squares fit.

Alkalinity was calculated from temperature, salinity,  $\text{pCO}_2$ ,  $\text{TCO}_2$ , and nutrient data using formulations described by Roy et al. (1993). Alkalinity also was calculated using methods and constants described in Peng et al. (1987) and Dickson and Millero (1987). A comparison between measured and calculated deep-water alkalinity from four different cruises in the Ross Sea indicated that constants from Roy et al. (1993) and measurements of  $\text{pCO}_2$ ,  $\text{TCO}_2$  give the best estimate of deep-water alkalinity.

## 2.5. *Nutrients*

In general, the methods employed for the bottle salinity, Winkler dissolved oxygen and nutrient analyses ( $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$  and  $\text{SiO}(\text{OH})_3^-$ ) did not differ significantly from those described in the JGOFS protocols distributed in 1994 (UNESCO, IOC Manual and Guides #29 reprinted as JGOFS (1996), and available on the web at: <http://usjgofs.whoi.edu/protocols.html>). Minor differences in procedure are noted by Gordon et al. (2000).

### 3. Computational methods

#### 3.1. Deficit calculations

To obtain estimates for NCP and nutrient drawdown during the bloom period we computed the carbon and nutrient deficits in the top 100 m between early spring and summer. The nutrient and  $\text{TCO}_2$  deficits ( $\text{Def}(X)$ ) ( $\text{mol m}^{-2}$ ) were calculated as the difference between the depth-integrated values made from the surface ( $z = 0$ ) to  $\sim 100$  m during the mid-summer cruise,  $X_{\text{summer}}$ , and those from the early spring cruise,  $X_{\text{spring}}$ , by the equation

$$\text{Def}(X_i) = \int_0^{100} (X_{\text{spring}}) dz - \int_0^{100} (X_{\text{summer}}) dz. \quad (1)$$

Substantial deficits for all variables were observed between the two seasons (Fig. 3). Although the mixed-layer depth at all stations was less than 60 m, we integrated through 100 m to account for deeper mixing during the early periods when the pycnocline was weaker and deeper.

Deficit calculations depend on three main assumptions: (1) that the early spring values for  $\text{CO}_2$  and nutrients are known, (2) ice production and melting were the only non-biological processes affecting nutrient concentrations in the Ross Sea, and (3) the effects of lateral and vertical transport on concentrations are negligible. Although potential alkalinity variations in surface water properties indicated the possibility of horizontal advection and diffusion in our study area, these anomalies were assumed to have been small compared to the changes brought about by ice melting. As such, we were able to correct for the ice melt by normalizing all nutrient and carbon values measured in this study to a constant salinity of 34.5, which was the mean salinity in the top 100 m of this area. The early spring values used in Eq. (1) for all stations south of  $76^\circ\text{S}$  and west of  $180^\circ$  (Fig. 1) were calculated using the average salinity-normalized values of nitrate, nitrite, and ammonia, (total inorganic nitrogen — TIN), phosphate, silicate,  $\text{TCO}_2$ , from 200 to 400 m at each station occupied between October 15 and 20, 1996 (Table 1). For stations east of  $180^\circ$  and north of  $76.0^\circ\text{S}$ , the deep-water values were more variable because of the occasional intrusion of warm Modified Circumpolar Deep Water (MCDW) (Jacobs et al., 1985; Jacobs and Giulivi, 1998). For these stations, we chose to only integrate down to the temperature minimum above the MCDW, which we assumed to be the extent of deep-winter mixing (Rubin et al., 1998).

#### 3.2. Carbon deficit corrections

The  $\text{CO}_2$  deficits [ $\text{Def}(\text{C})$ ] measured in the water column have three components: photosynthesis/respiration, exchange with atmospheric  $\text{CO}_2$ , and precipitation/dissolution of  $\text{CaCO}_3$ . In order to calculate NCP, corrections for the effects of gas exchange and precipitation/dissolution of  $\text{CaCO}_3$  must be made. We used the changes in the “potential” alkalinity (Brewer and Goldman, 1978), which is defined as

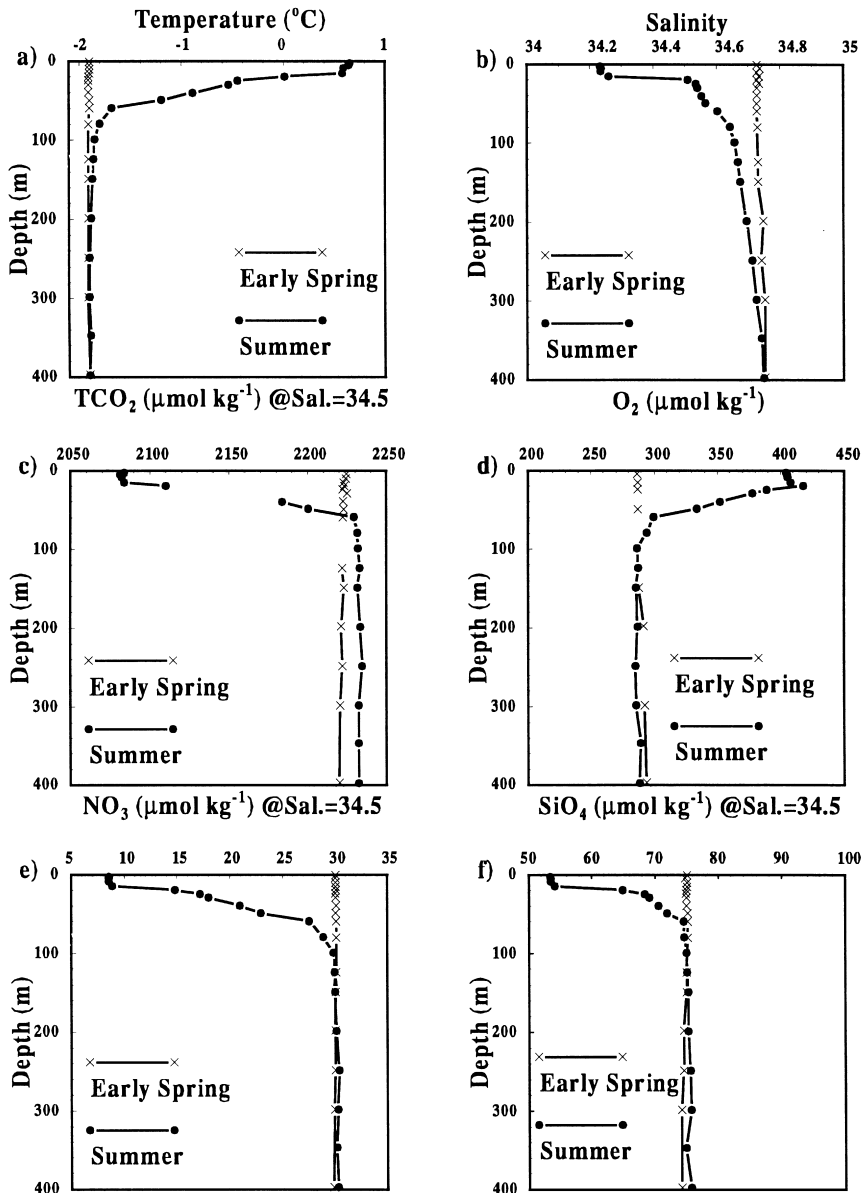


Fig. 3. Representative vertical profiles of (a) temperature, (b) salinity, (c) total dissolved carbon dioxide, (d) dissolved oxygen, (e) nitrate, and (f) silicic acid collected during the early spring (Station 10, sampled October 10, 1996;  $\times$ ) and summer cruises (Station 1, sampled January 13, 1997;  $\bullet$ ) at  $76^{\circ}30'S$  and  $169^{\circ}00'E$ . All concentrations normalized to a salinity of 34.5.

the sum of alkalinity and  $\text{NO}_3^-$ . This technique will account for increases in alkalinity caused by photosynthetic utilization of  $\text{NO}_3^-$ . The composite profiles of salinity-normalized potential alkalinity (Fig. 4) from the early spring and summer cruises

Table 1

Early spring values calculated from the average nutrient,  $\text{TCO}_2$  and organic carbon measurements made between October 15 and 20, 1996 from depths of 100–400 m. Density profiles showed that mixed layer depths extended as far as 400 m during this time interval. All values normalized to a salinity of 34.5

Parameter	Early spring value
$\text{TCO}_2$	$2287 \mu\text{mol l}^{-1}$
$\text{PO}_4$	$2.19 \mu\text{mol l}^{-1}$
$\text{SiO}(\text{OH})_3^-$	$75.9 \mu\text{mol l}^{-1}$
TIN	$31.3 \mu\text{mol l}^{-1}$
DOC	$42 \mu\text{mol l}^{-1}$
POC	$2.2 \mu\text{mol l}^{-1}$

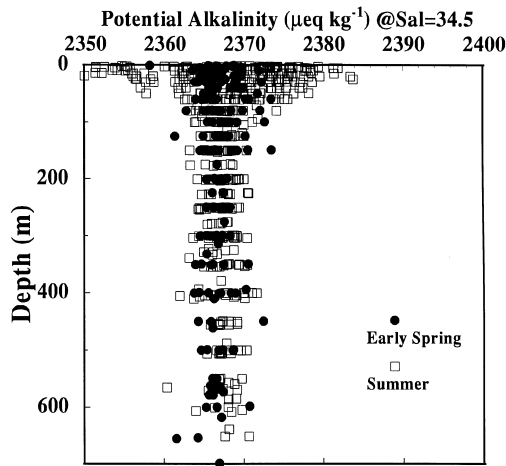


Fig. 4. Salinity-normalized potential alkalinity (sum of alkalinity plus nitrate) during early spring (●) and summer (□). Early spring cruise alkalinity was measured and summer cruise alkalinity was calculated from measurements of  $\text{TCO}_2$  and  $\text{pCO}_2$  using Roy et al. (1993).

illustrate that variations in alkalinity are less than  $4 \mu\text{eq kg}^{-1}$  below 100 m and as much as  $16 \mu\text{eq kg}^{-1}$  at the surface during the austral summer.

Although the variation in salinity-normalized potential alkalinity at the surface was large compared to variation in the deep water, these variations were small compared to the deficit in  $\text{TCO}_2$  observed at the surface and therefore not accounted for in the calculation of NCP. If precipitation or dissolution of  $\text{CaCO}_3$  were the source of the variation in potential alkalinity, this would imply changes in the  $[\text{CO}_3^{2-}]$  of the surface water. Both the appearance of *pteropods* in sediment traps (Collier et al., 2000) and the observation of increases in alkalinity in surface waters due to dissolution of  $\text{CaCO}_3$  during the melting of sea ice (Richardson, 1976; Tan et al., 1983; Anderson and Jones, 1985) indicated that  $\text{CaCO}_3$  precipitation or dissolution was the source of the high variation in surface potential alkalinity. For each mole of  $\text{Ca}^{2+}$  ion

added to the surface water by dissolution there will be a change in alkalinity of 2 eq. This ratio implies that a  $\pm 16 \mu\text{eq kg}^{-1}$  variation in potential alkalinity would cause an  $\pm 8 \mu\text{mol kg}^{-1}$  variation in surface  $\text{TCO}_2$ . This variation is a small fraction (5%) of the seasonal deficit in  $\text{TCO}_2$  measured at the surface (ca.  $160 \mu\text{mol kg}^{-1}$ ). It is also possible that other water masses with potential alkalinities different from those in the deep water are being laterally advected into the study area. Measurements obtained during AESOPS cruises in the Ross Sea did not indicate that the deviations in potential alkalinity are concurrent with other water mass properties (i.e. salinity, temperature or nutrients) or locations in the Ross Sea. With no identifiable source of either high- or low-surface salinity-normalized potential alkalinity, it seems unlikely that lateral advection is the cause of the variation observed in the surface waters. Past studies also have shown variation in surface salinity-normalized potential alkalinity of  $\pm 10 \mu\text{eq kg}^{-1}$  in the Ross Sea (Bates et al., 1998) and in the Ross Gyre (Rubin et al., 1998) and also have pointed out that the alkalinity variations due to  $\text{CaCO}_3$  precipitation or dissolution is small compared to the magnitude of the  $\text{TCO}_2$  draw-down.

Measured  $\text{TCO}_2$  also must be corrected for gas exchange before the deficit of  $\text{TCO}_2$  due to NCP can be calculated. The gas exchange fluxes were estimated based on the  $\text{CO}_2$  gas transfer coefficient across the sea surface and the difference between atmospheric  $\text{pCO}_{2(\text{atm})}$  and surface seawater  $\text{pCO}_{2(\text{sw})}$ . The gas transfer coefficient is taken to be a function of wind speed (Wanninkhof, 1992). Local wind speeds averaged over the last five years have been compiled by National Center for Environmental Prediction-National Center for Atmospheric Research (NCEP-NCAR) (Lamont Climate Group Library – <http://rainbow.ldeo.columbia.edu>). These data indicate that during the months of open water (mid-November through late-February), average wind speed,  $u_{\text{av}}$ , rarely exceeds  $3 \text{ m s}^{-1}$ . Appropriate to these low average monthly wind speeds is the gas transfer coefficient of Wanninkhof (1992)

$$k = 0.39u_{\text{av}}^2 (\text{Sc}/660)^{-0.5}, \quad (2)$$

where  $k$  ( $\text{cm h}^{-1}$ ) is the gas transfer velocity and  $\text{Sc}$  is the Schmit number, which is a dimensionless function of temperature and salinity. Although this relationship has been found to be consistent with the direct measurements obtained during the recent Gas Ex-98 field study using an eddy-correlation method (Wanninkhof and McGillis, 1999), errors resulting from the non-linear relationship between wind speed and gas transfer velocity can lead to underestimates of average transfer velocities in regions with highly variable wind speeds. Because of the high standard deviation for wind speeds in both space and time, the transfer velocity in the Southern Ocean may be underestimated using Eq. (2) (Boutin and Etcheto, 1991). The net sea-air  $\text{CO}_2$  flux was calculated using the solubility ( $s$ ) of  $\text{CO}_2$  gas in seawater (Weiss, 1974).

$$F_{\text{CO}_2} = ks(\Delta\text{pCO}_2), \quad (3)$$

$$\Delta\text{pCO}_2 = \text{pCO}_{2(\text{sw})} - \text{pCO}_{2(\text{atm})}. \quad (4)$$

A time-integrated flux ( $\int(F_{\text{CO}_2}) dt$ ) was calculated using monthly wind data and daily  $\Delta\text{pCO}_2$  from November 11, when remote-sensed microwave data indicated ice

melt should begin in the Ross Sea (Jacobs and Comiso, 1989), to the time that the samples were collected. As stated earlier, for each day between the early spring and summer cruises  $\Delta p\text{CO}_2$  was calculated by fitting measurements made at each station to a sine function. Assuming that alkalinity plays a insignificant role in the Ross Sea carbon budget, NCP can be calculated from the deficit of total  $\text{CO}_2$  (Def(C)) minus the gas flux ( $\int(F_{\text{CO}_2}) dt$ ) to the atmosphere by the following equation:

$$\text{NCP} = \text{Def(C)} - \int(F_{\text{CO}_2}) dt. \quad (5)$$

The magnitude of this correction ranges from 2 to 10% of the  $\text{CO}_2$  deficit. Since the  $p\text{CO}_{2(\text{sw})}$  was below atmospheric values, the net flux was into the ocean, making the NCP 2–10% greater than the  $\text{CO}_2$  deficit indicates. It also must be noted that because of uncertainty in the transfer velocity in the Southern Ocean we estimate that our evaluation of  $\int(F_{\text{CO}_2}) dt$  could be as much as 30% too low.

### 3.3. Organic carbon production

The surpluses in DOC, POC and TOC (DOC + POC) [Surp(XOC)] through 100m were calculated according to the following equation using values from Table 1 for the early spring values and the summer values.

$$\text{Surp}(X_i) = \int_0^{100} (X_i(\text{summer})) dz - \int_0^{100} (X_i(\text{winter})) dz. \quad (6)$$

## 4. Results and discussion

Three regions were delineated by their physical and chemical characteristics and the magnitude of nutrient and  $\text{CO}_2$  reduction through the process of photosynthesis (Fig. 1, Tables 2 and 3). The low values in underway  $p\text{CO}_2$  measurements (Fig. 2) most clearly define the extent of the boundaries for Regions I and II, while the higher values of  $p\text{CO}_2$  define Region III. The boundaries of each area have been chosen to be as consistent as possible with those chosen by Nelson et al. (1996), who used similar regional divisions.

### 4.1. Region I

During the mid-summer cruise, the southwestern area (Region I, Fig. 1) had shallow mixed layers (mean = 26 m), substantial TOC accumulations (Fig. 5), the largest silicate reductions (Fig. 6a), and relatively high NCP values (mean =  $6.7 \pm 1.7 \text{ mol C m}^{-2}$ ; Fig. 6b). The shallow mixed layer and the high silicate reductions in this area are indicative of ice-edge blooms that have been observed throughout the Southern Ocean (El-Sayed and Taguchi, 1981; Jennings et al., 1984; Smith and Nelson, 1986, 1990). These past studies indicate that the ice-edge bloom plays an important role in productivity because the regime represents an intensely productive

Table 2

Biologically driven deficits of silicic acid (Def(Si)), carbon (NCP) and the Def(Si)/NCP ratio found at each station occupied during the summer cruise

Station	Latitude (°N)	Longitude (°E)	Date	Def(Si) (mol m <sup>-2</sup> )	NCP (mol m <sup>-2</sup> )	Def(Si)/NCP
Region I						
1	- 76.499	169.004	1/13/97	0.68	4.872	0.140
13	- 76.501	168.997	1/27/97	0.82	5.790	0.142
26	- 76.503	169.005	2/6/97	0.46		
27	- 76.188	163.338	2/6/97	0.93	8.688	0.107
28	- 76.500	168.987	2/8/97	0.50	7.463	0.066
Region II						
2	- 76.498	169.992	1/15/97	0.62		
3	- 76.502	172.011	1/15/97	0.11	7.784	0.015
4	- 76.498	173.997	1/16/97	0.23	8.601	0.027
5	- 76.500	176.003	1/16/97	0.23	7.919	0.029
6	- 76.499	177.993	1/18/97	0.18	5.562	0.032
7	- 76.492	179.998	1/18/97	0.29		
9	- 78.050	183.936	1/21/97	0.21	9.980	0.021
10	- 76.499	175.997	1/22/97	0.24	6.788	0.036
14	- 76.492	170.032	1/29/97	0.35		
15	- 76.500	172.017	1/29/97	0.36	10.785	0.033
16	- 76.501	174.003	1/29/97	0.40	5.840	0.069
17	- 76.498	175.999	1/30/97	0.32	7.225	0.045
18	- 76.503	178.010	1/31/97	0.16	5.280	0.030
19	- 76.498	179.998	1/31/97	0.28		
23	- 77.998	183.997	2/3/97	0.72	8.219	0.087
24	- 77.405	176.005	2/4/97	0.64	9.490	0.068
25	- 76.501	175.991	2/4/97	0.37	4.437	0.083
Region III						
8	- 76.501	- 178.002	1/19/97	0.31	2.655	0.117
11	- 74.003	176.997	1/23/97	0.36	2.043	0.174
12	- 74.332	- 175.996	1/26/97	0.37	1.204	0.309
20	- 76.500	- 178.003	2/1/97	0.37	3.014	0.124
21	- 75.503	- 177.997	2/2/97	0.52	2.270	0.227
22	- 76.501	- 173.999	2/3/97	0.44	4.230	0.104

Table 3

Average NCP for each biogeochemical regime in the Ross Sea. The daily NCP is a regional average of daily NCP over the time interval starting from October 18, 1996 to the time each station was occupied during the summer cruise

Region	Area (km <sup>2</sup> )	NCP (mol m <sup>-2</sup> )	NCP (Tg C)	Daily NCP (g C m <sup>-2</sup> d <sup>-1</sup> )	Def(Si)/NCP
I	52,000	6.7 ± 1.7	4.2 ± 1.0	0.8 ± 0.1	0.11 ± 0.04
II	155,000	7.5 ± 1.9	14.0 ± 3.6	0.9 ± 0.2	0.04 ± 0.02
III	234,000	2.6 ± 1.0	7.2 ± 2.9	0.3 ± 0.1	0.18 ± 0.08
Total	441,000	4.8 ± 1.9	25 ± 10		

ecosystem common to the Southern Ocean (Cunningham and Leventer, 1998). Until ice-edge blooms were observed, it was hard to explain the thick deposits of biogenic siliceous sediments on the Antarctic shelves as well as the large populations of higher trophic level animals (e.g. penguins) often associated with the ice (DeMaster, 1981; Ainley and Jacobs, 1981). Since then, several studies have contributed to our understanding of ice-edge blooms. Most importantly, ice-edge blooms seem to be dominated by diatoms (Jennings et al., 1984; Smith and Nelson, 1985, 1990; Smith et al., 1996; Cunningham and Leventer, 1998). There also seems to be a link between the epontic and the dominant pelagic algae (i.e. *Fragilariopsis curta*) in the water. It further appears that diatoms can maintain a primary productivity as high as  $1.3 \text{ g C m}^{-2} \text{ d}^{-1}$  in the shallow mixed layers near melting ice edges (Smith and Nelson, 1985; Wilson et al., 1986; Smith et al., 1996; Leventer and Dunbar, 1996). In addition, sediment trap data have indicated that these diatom blooms also may be effectively exported from the mixed layer via fecal pellet production by metazoan grazing (Smith and Dunbar, 1998; Dunbar et al., 1998) and the rapid settling of diatoms (Leventer and Dunbar, 1996).

In our study the average Def(Si)/NCP ratio in the southwestern Ross Sea (Region I) was  $0.11 \pm 0.04$ . This ratio is consistent with cultures of subtropical diatoms, which have an average Si/C ratio of 0.13 (Brzezinski, 1985). In contrast, Nelson et al. (1996) and Smith et al. (1996) found slightly greater Si/C ratios from suspended particulate and isotopic incorporation studies in this part of the Ross Sea. In a compilation of two cruises done in January 1990 and February 1992, Smith et al. (1996) found the mean biogenic silica to POC ratio was 0.41 ( $n = 72$ ). In an independent study, which included data from January 1990 and February 1992 in addition to data from December 1994, Nelson et al. (1996) found the uptake ratio of silica to carbon in this area of the Ross Sea during incubation studies to be 0.23. The anomalously high Si/C values of Smith et al. (1996) and Nelson et al. (1996) have been supported by even higher values calculated during the austral summer of 1983. During the 1983 study the mean particulate biogenic silica to POC ratios for the southwestern Ross Sea were 0.62 (Smith and Nelson, 1985) and uptake ratios averaged 0.57 (Nelson and Smith, 1986). These values were similar to Def(Si)/NCP ratio of  $0.66 \pm 0.02$  calculated for the northern limb of the Ross Gyre (Rubin et al., 1998), indicating that this annual variability in the Si/C ratio might be due to changes in the micro-nutrient concentrations. Recent observations by Takeda (1998) and Hutchins and Bruland (1998) show a significant increase in the Si/C ratio of diatoms as a result of iron deficiency. It is possible that the bloom observed during our study was iron replete and therefore had Si/C ratios nearer those of the subtropical diatoms observed by Brzezinski (1985), while in other years the southwestern Ross Sea was iron depleted like the Ross Gyre, as demonstrated by Martin et al. (1990). It is also possible that higher than normal *Phaeocystis* growth in this area contributed to the low Def(Si)/NCP ratio.

Net community production in the southwestern region ranged from  $4.8 \text{ mol C m}^{-2}$  in the eastern boundary to  $8.7 \text{ mol C m}^{-2}$  in the vicinity of the near-shore fast ice to the west. The mean daily net production rate for the period starting October 18, 1996 was  $0.8 \pm 0.1 \text{ g C m}^{-2} \text{ d}^{-1}$ . In a similar ice-edge bloom found in the Weddell Sea, Jennings et al. (1984) calculated production using summer deficits of  $\text{NO}_3^-$  at ca.  $0.57 \text{ g C m}^{-2} \text{ d}^{-1}$  with an assumed C/N ratio of 5.6. If a C/N ratio of 6.6 by Redfield

et al. (1963) is used, the Jennings et al. (1984) production rate would increase to  $0.67 \text{ g C m}^{-2} \text{ d}^{-1}$ , similar to our observations in the Ross Sea. Other estimates in the Ross Sea using seasonal nutrient and  $\text{TCO}_2$  reduction have not included ice-edge conditions; however, daily uptake measurements using radioisotopes of carbon illustrate that these uptake rates were similar to other studies. Wilson et al. (1986) found the  $^{14}\text{C}$ -based productivity in the southwestern regime to be  $0.96 \text{ g C m}^{-2} \text{ d}^{-1}$  in late January and early February, while Smith et al. (1996) found mean productivity in the southern Ross Sea to range from 2.63 ( $n = 22$ ) in mid-January to  $0.78 \text{ g C m}^{-2} \text{ d}^{-1}$  ( $n = 19$ ) in mid-February. Given the physical and chemical conditions encountered by our study, we suggest that this region was dominated by diatoms that grow in a strongly stratified water column similar to other ice-edge regimes observed throughout the continental shelf of Antarctica.

#### 4.2. Region II

Region II (Fig. 1), of the southern Ross Sea, had different environmental characteristics than found in the southwestern region (Fig. 5). Region II had deeper mixed layers (mean = 43 m), the greatest reductions in  $\text{TCO}_2$ , and the largest accumulations of TOC. Drawdown of dissolved silica, however, was minor relative to other areas in the Ross Sea (Fig. 6a and Table 2). This region has previously been observed to be the site of extensive blooms of the colonial haptophyte *Phaeocystis antarctica* (Smith and Gordon, 1997), and microscopic observations confirmed this to be true during this study as well (S. Mathot and D. Caron, personal communication). Although *Phaeocystis* regimes are common in the Ross Sea (Nelson et al., 1996; Smith et al., 1996), they also have been observed in the Weddell Sea (Fryxell and Kendrick, 1988) and Bransfield Strait (Bodungen et al., 1986). These regimes not only are distinguished by high productivity (Smith and Gordon, 1997), but also by relatively deep mixed layers (Bodungen et al., 1986; DiTullio and Smith, 1996; Arrigo et al., 1998, 1999). The mixed layers in Region II are deep because this region is affected by strong katabatic winds coming off the Ross Ice Shelf (Zwally et al., 1985; Kurtz and Bromwich, 1985, 1985; Jacobs and Comiso, 1989). Arrigo et al. (1998) pointed out that early in the season the wind forcing in this area may be too large to sustain any population; however, with increased solar irradiation at the onset of the spring, the water column eventually stratifies enough to provide a habitat for *Phaeocystis*. The deeper mixed layers allow a species with higher photosynthetic efficiencies to dominate. Palmisano et al. (1986) observed a 3–4-fold increase in photosynthetic efficiency in a *Phaeocystis* bloom as it was advected under sea ice in East McMurdo Sound in a period of 4 days. This study also showed that the *Phaeocystis* under the ice exhibited considerably higher photosynthetic efficiencies than diatoms at similar light levels (Hoepffner, 1984). This finding would indicate that *Phaeocystis* adapts better to the low-light conditions in areas with deeper mixed layers such as wind-exposed polynyas. Arrigo et al. (1998) also have suggested that continued surface warming will decrease the mixed layer to depths that allow diatoms to have a competitive advantage. Our results show that the  $\text{Def}(\text{Si})/\text{NCP}$  and  $\text{Def}(\text{Si})$  significantly increased on the second re-occupation during the summer cruise in several locations throughout this region, indicating that

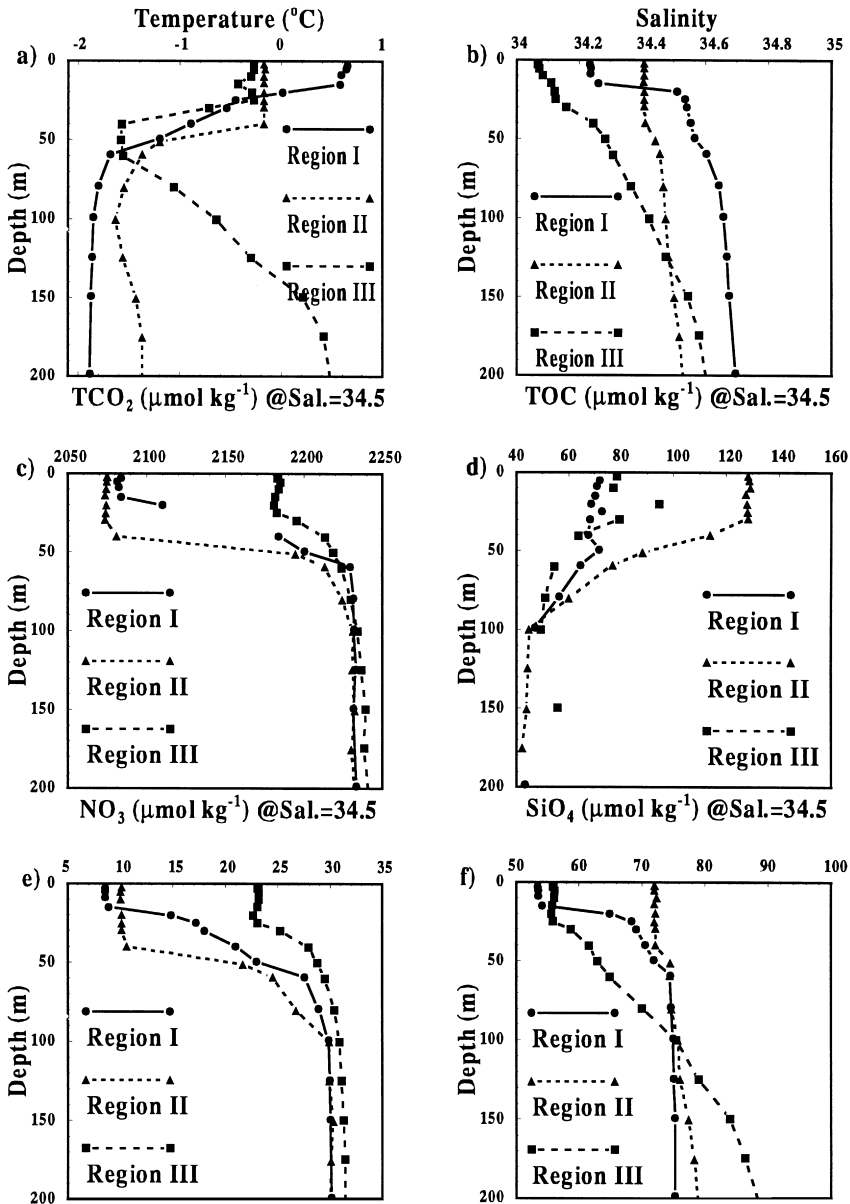


Fig. 5. Representative vertical profiles of (a) temperature, (b) salinity, (c)  $\text{TCO}_2$ , (d) TOC, (e) nitrate, and (f) silicic acid from the three biogeochemical regions. The profiles represent summer conditions from which net community production can be estimated.

the diatoms continued to utilize  $\text{TCO}_2$  after *Phaeocystis* growth had slowed or ceased (Figs. 6b and c). These observation may explain why the peak of production in the *Phaeocystis*-dominated region was reported in mid-December (Nelson et al., 1996 and

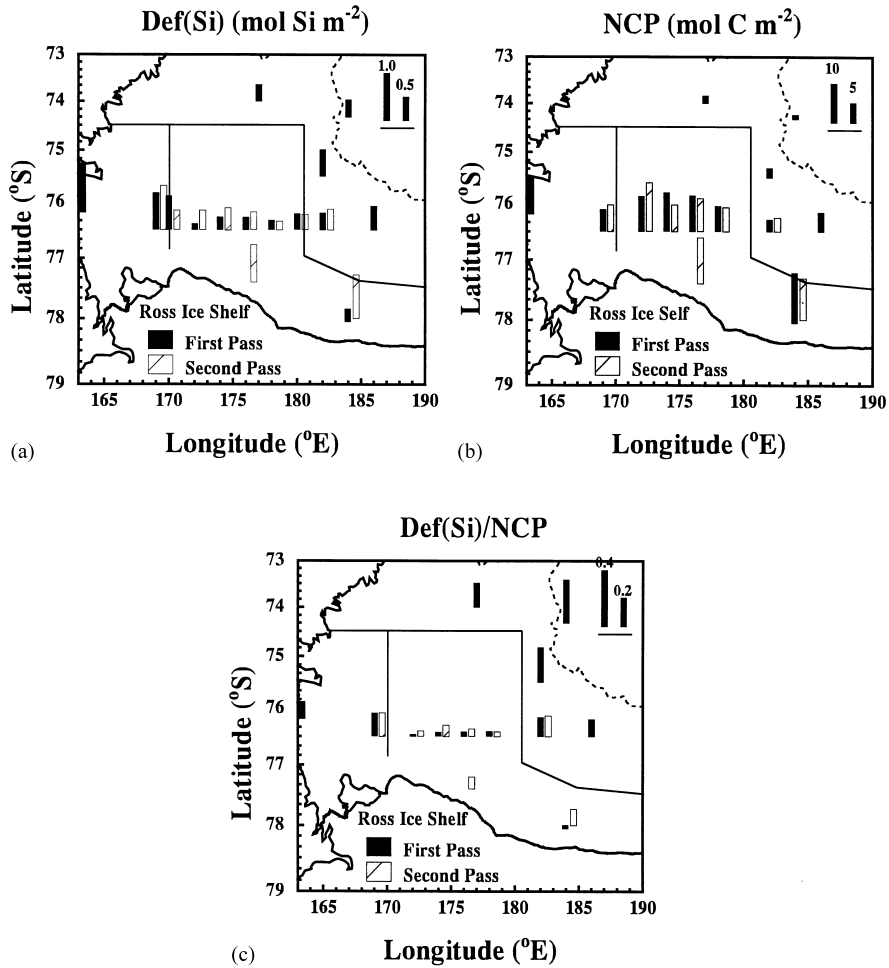


Fig. 6. Changes between mid-October and mid-February in (a) silicic acid ( $\text{mol m}^{-2}$ ), (b) net community production (NCP;  $\text{mol m}^{-2}$ ), and (c) Def(Si)/NCP. Solid bars represent the first occupation during summer cruise, and the open bars represent the second occupation.

Smith and Dunbar, 1998) and the maximal flux of diatoms to the near-bottom sediment traps was reported in late February (Leventer and Dunbar, 1996; Smith and Dunbar, 1998; Dunbar et al., 1998).

NCP calculated in this area was between 4.4 and 10.8  $\text{mol C m}^{-2}$  (Fig. 6b) and the mean daily NCP averaged  $0.9 \pm 0.2 \text{ g C m}^{-2} \text{ d}^{-1}$  for the period from late October to early February. From mid-November through early December 1994, Smith and Gordon (1997) estimated new production to be  $1.52 \text{ g C m}^{-2} \text{ d}^{-1}$  in the central Ross Sea polynya from the change in nitrate concentrations above 100 m and a Redfield ratio of 6.6. Bates et al. (1998), using surface measurements of  $\text{TCO}_2$  and profiles of TIN, estimated daily NCP rates of  $0.86 \text{ g C m}^{-2} \text{ d}^{-1}$  during the same bloom period as

Smith and Gordon (1997). Bates et al. (1998) also estimated daily NCP of  $0.98 \text{ g C m}^{-2} \text{ d}^{-1}$  in late December 1995. Our estimate of the mean daily productivity includes the early season period when rates were probably extremely small; yet our rates are comparable to the those observed by Bates et al. (1998) during the peak of the bloom. This may indicate that the *Phaeocystis* bloom observed during our study from mid-January through mid-February of 1997 had much higher rates of primary productivity than found in past studies.

#### 4.3. Region III

The northern area, Region III (Fig. 1), had shallow mixed-layer depths ( $\sim 27 \text{ m}$ ), the smallest reductions of TIN and  $\text{CO}_2$ , and the smallest accumulations of TOC (Figs. 2 and 5). Moderate Def(Si) and high Def(Si)/NCP ratios ( $0.18 \pm 0.08$ ) (Figs. 6a and c) also were observed. Although the Def(Si)/NCP ratios were greater than those observed in Regions I and II, they were still much smaller than those measured by Rubin et al. (1998) and Smith et al. (1996). The silica profile (Fig. 5f) in Region III showed a gradient unlike other areas because it continued to increase to 200 m due to an intrusion of high-silicate water from off the shelf. This high-silicate water has been identified as modified circumpolar deep water (MCDW) (Jacobs and Giulivi, 1998) originating from lower circumpolar deep water (LCDW) beyond the shelf break (Locarnini, 1994). The intruding MCDW had low salinity (between 34.5 and 34.6) and warmer temperatures (above  $-1.5^\circ\text{C}$ ) at Station 11 below 100 m (Fig. 5). At this station a temperature minimum, close to the freezing temperature of seawater, was observed just above the warm MCDW. This low-temperature water represents remnant surface winter water and suggests that the deep convective mixing, which may have been prevalent in other areas during the winter, did not occur in this area. Hence, the early spring values of nutrients and inorganic carbon at stations in Region III are represented by those observed in the remnant winter mixed layer. The NCP (between  $1.2$  and  $4.2 \text{ mol C m}^{-2}$ ) and daily production rates were found to be the lowest of all three areas.

The nitrate and silica profiles both showed that the concentrations present were in excess (relative to physiological uptake capabilities; Smith and Harrison, 1991; Nelson et al., 1995), but it is unclear why the nutrient removal did not proceed further. Nelson et al. (1996) have pointed out that the winter ice cover over Region III disappears much later than Regions I and II, similar to the eastern border of the continental shelf (Arrigo et al., 1998). Another factor that may contribute to this low productivity is a lack of micronutrients such as Fe. Based on Takeda's (1998) results, the high Def(Si)/NCP ratio would support this possibility. Although Martin et al. (1990) observed iron-limited growth during the summer in the Ross Sea for much of the area, iron stimulation was greatest off the shelf in the Ross Sea gyre. It is likely that this region is strongly influenced by waters from beyond the shelf break, and hence it might be expected that both trace metal concentrations and NCP would be reduced. Most likely it is a combination of both factors (limitation by irradiance when ice is present and limitation by trace metals after the ice melts) that reduces seasonal production in the northern regime.

#### 4.4. Export and deep-water enrichment

If the effects of diapycnal mixing from below and horizontal advection on the mixed-layer chemistry are assumed to be negligible, the NCP estimated should represent an integral of photosynthesis (production of organic carbon) minus the respiration (oxidation of organic carbon) for the biological community over the depth of integration between the time of the early spring and summer cruises. A daily estimate of NCP over this same period should then represent average daily net production of organic carbon. The amount of organic carbon exported from the upper 100 m was estimated from the Surp(TOC)/NCP ratio, which is a measure of the fraction of CO<sub>2</sub> fixed by photosynthesis but remaining in the upper 100 m of the water column. Therefore, the fraction of carbon exported can be quantified from the following:

$$\text{Export fraction} = 1 - \text{Surp(TOC)/NCP.} \quad (7)$$

At most of the stations the fraction of the NCP that existed as TOC in the upper 100 m decreased or remained the same during the re-occupation, suggesting that additional export had occurred as the bloom progressed (Fig. 7). The decrease in Surp(TOC)/NCP with the progression of the bloom was further emphasized by the low Surp(TOC)/NCP ratios calculated for stations occupied along the Ross Ice Shelf

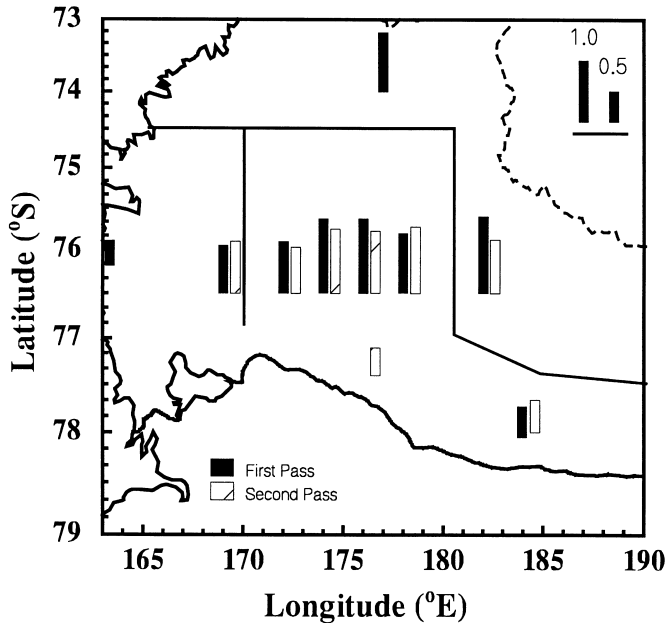


Fig. 7. Ratio of surplus total organic carbon Surp(TOC) to net community production (NCP) in the Ross Sea. Solid bars represent the first occupation during the summer cruise, and the open bars represent the second occupation.

and near shore (Fig. 7), which showed extremely high NCP's but very low primary production (Smith et al., 2000), indicating senescence of the bloom.

Further analysis of the Surp(TOC) versus NCP indicated that both *Phaeocystis* (Def(Si)/NCP < 0.1) and diatom (Def(Si)/NCP > 0.1) dominated stations are capable of exporting a large fraction of the NCP (> 50%) below 100m (Fig. 8). This is supported by sediment trap data from previous studies in the Ross Sea, which suggested equivalent fractions of carbon are exported in diatom- and *P. antarctica*-dominated areas (Smith and Dunbar, 1998; Dunbar et al., 1998). However, Fig. 8 suggests that the *Phaeocystis*-dominated stations do not export a very high fraction of NCP until NCP exceeds  $6 \text{ mol m}^{-2}$ . The observation that a larger fraction of diatoms were exported at a low NCP indicates that there may be a species-specific process that facilitates export of diatoms at a lower biomass or at an earlier time in the bloom period. Rapid aggregation of diatoms (Smetacek, 1985; Alldredge and Gotschalk, 1989; Riebesell, 1991; Wassmann et al., 1996; Barlow et al., 1998) could be the cause of the early export of diatoms during a bloom. Riebesell (1991) points out that among other factors controlling aggregation, “stickiness”, size and concentration are the most important characteristics. In the case of chain-forming and spined species of diatoms, there is a much higher probability of aggregate formation leading to more export at lower biomass. Similar aggregate formation has been suggested in a few instances for *Phaeocystis* (Wassmann et al., 1990; Asper and Smith, 1999), but this process presumably needs a much higher biomass to initiate export, as we have observed from the fact that only stations with high NCP show an export fraction > 0.5 (Fig. 8). Past sediment trap studies in the Ross Sea have noted that

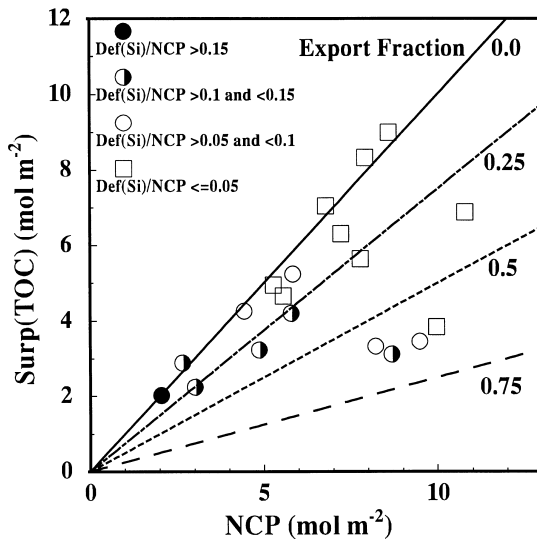


Fig. 8. Surp(TOC) as a function of NCP. Lines represent the exported fraction of NCP ( $1 - \text{Surp(TOC)}/\text{NCP}$ ). Stations represented by solid circles or half filled circles had a Def(Si)/NCP ratio greater than 0.1, suggesting that they were diatom-dominated. Stations represented by open circles and squares had Def(Si)/NCP ratios less than 0.1, suggesting a *Phaeocystis*-dominated regime.

*Phaeocystis*-dominated areas in the Ross Sea are associated with loosely bound “algal flocs” or aggregates while diatoms blooms have been associated with fecal pellet sedimentation (DiTullio and Smith, 1996; Smith and Dunbar, 1998; Dunbar et al., 1998). These studies have further noted that fecal pellet sink faster than alga flocs and loose aggregates, which offers another mechanism for the earlier export of diatoms.

On average during the summer cruise,  $84 \pm 25\%$  of the NCP still existed as TOC in the upper 100 m of the water column, while the balance ( $16 \pm 25\%$ ) had been exported to the deep water (Table 4). If only Regions I and II are considered,  $27 \pm 25\%$  of the NCP was exported to below 100 m. This estimate of export was supported by enrichment of  $\text{TCO}_2$  found in the deep water from 100 to 500 m (Fig. 3c). By taking the difference between the deep-water  $\text{TCO}_2$  integrated from 100 to 500 m during the early spring and that during the summer, we found an average enrichment of  $2.2 \pm 0.9 \text{ mol m}^{-2}$  in Regions I and II. With a combined average export of  $2.0 \pm 1.0 \text{ mol m}^{-2}$  in Regions I and II, it appears that most of the exported NCP was remineralized between 100 and 500 m. Deep-water remineralization could not be calculated for Region III because of complications due to the intrusion of modified circumpolar deep water and because the value of the deep-water  $\text{TCO}_2$  was not measured at any stations in this region during the early spring cruise.

Although the deep-water  $\text{TCO}_2$  enrichment during the summer is matched by export of organic carbon below 100 m in Regions I and II, there is no concurrent enrichment in nutrients nor is the enrichment profile what might be expected. At depth between 200 and 400 m, the average deep-water enrichment of  $\text{TCO}_2$  ( $\sim 7 \mu\text{mol kg}^{-1}$ ) was clearly larger than the standard deviation of  $\text{TCO}_2$  measurements ( $\sim 2.5 \mu\text{mol kg}^{-1}$ ) in the deep water (Fig. 3c). Assuming the Redfield ratio of 106/16 for C/N, we would expect an enrichment of  $1.1 \mu\text{mol kg}^{-1}$  of TIN to match the  $7 \mu\text{mol kg}^{-1}$  increase in  $\text{TCO}_2$  between 200 and 400 m. Similarly, the  $\text{PO}_4$  should be enriched by  $0.07 \mu\text{mol kg}^{-1}$  during the summer cruise. Although no increase was seen in the average deep-water value of either nutrient, the standard deviation of these averages ( $\pm 0.5$  and  $\pm 0.07$  for TIN and phosphate, respectively) suggests that the large variability in deep water may mask small changes predicted for nutrient enrichment. This was further shown in an analysis of repeat stations occupied in the Pacific during the world ocean circulation experiment (WOCE), which implied that, using sampling and measurement techniques similar to those used during this

Table 4

Average deep-water enrichment of salinity-normalized  $\text{TCO}_2$  between the early spring and summer cruises from 100 to 500 m. Surp(TOC)/NCP and Surp(DOC)/NCP represent the fractions of NCP that exist as organic carbon (TOC and POC), respectively, from 0 to 100 m. Average values are areawise weighted

Region	Deep-water enrichment ( $\text{mol m}^{-2}$ )	Surp (TOC)/NCP	Surp (DOC)/NCP	Export (%)
I	$2.3 \pm 0.9$	$0.58 \pm 0.20$	$0.08 \pm 0.05$	33–64
II	$2.1 \pm 0.9$	$0.78 \pm 0.26$	$0.16 \pm 0.05$	0–64
III		$0.94 \pm 0.18$	$0.23 \pm 0.07$	0–25
Average		$0.84 \pm 0.26$	$0.19 \pm 0.07$	$16 \pm 25$

experiment, deep-water values of nitrate and phosphate can be offset by 0.9 and  $0.06 \mu\text{mol kg}^{-1}$  (Takahashi et al., 1998), respectively, in areas considered to be dynamically quiescent. Although oxygen should be helpful in confirming the regeneration of exported organic carbon between 100 and 500 m, it was not considered in this analysis because of its high variation from intrusions of modified circumpolar deep water. The ammonia concentration, on the other hand, is not effected by MCDW and does show considerable enrichment from early spring to summer. The enrichment of ammonia peaks in the mixed layer and decreases with depth to an undetectable level at 400 m (Gordon et al., 2000). This decrease in enrichment with depth is not observed in the  $\text{TCO}_2$  measurements as would be expected. Instead, the offset in salinity normalized deep-water  $\text{TCO}_2$  is constant throughout the water column (Fig. 3c), indicating that the  $\sim 7 \mu\text{mol kg}^{-1}$  increase in  $\text{TCO}_2$  from early spring to summer may be a systematic error that was not corrected for in the standard inter-comparison.

Based on analysis of the salinity normalized deep-water  $\text{TCO}_2$  throughout the Ross Sea, it is unlikely that the enrichment is due to intrusion of water masses enriched in  $\text{TCO}_2$ . This was shown by the deep-water salinity normalized  $\text{TCO}_2$  observed during cruises done in the autumn of 1997 (Gordon et al., 2000) which indicate that deep-water  $\text{TCO}_2$  values did not change after the summer cruise. This finding suggests that if remineralization of exported material was the source of the enrichment, further remineralization ceased to happen after summer occupation of the Ross Sea. This finding is counterintuitive considering Sweeney et al. (2001) who show a large increase in export between the summer and autumn occupation of the Ross Sea, suggesting that enrichment in deep-water  $\text{TCO}_2$  should have increased dramatically during the autumn occupation of the Ross Sea. In summary, it is fortuitous that export of carbon from the upper 100 m of the water column matches the enrichment of  $\text{CO}_2$  from 100 to 500 m, but the fate of the exported carbon in the water column must be carefully assessed in light other factors that suggest a systematic error in early spring  $\text{TCO}_2$  observations. While this offset makes a large difference in understanding the fate of exported organic carbon, it only makes very small differences ( $\sim 10\%$ ) in the magnitude of NCP and the export out of the 100 m of the water column.

As demonstrated, the  $\text{Surp}(\text{TOC})/\text{NCP}$  ratio can be used to estimate the fraction of NCP exported out of the top 100 m of the water column over the course of our study (through early February). By the same method the  $\text{Surp}(\text{DOC})/\text{NCP}$  ratio can be used to estimate a potential carbon export by assuming that all of the particulate carbon eventually will sink out of the mixed layer, leaving only the excess DOC to be remineralized in the mixed layer. The average  $\text{Surp}(\text{DOC})/\text{NCP}$  for all the stations occupied during the summer cruise of  $0.19 \pm 0.07$  is similar to the value of  $0.14 \pm 0.09$  estimated by Hansell and Carlson (1998) in the Ross Sea during the 1994 growing season. This value implies that as much as  $81 \pm 7\%$  of the NCP has the potential for export as POC from the upper 100 m of the water column by the end of the growing season. The remaining excess DOC is considered labile and will be remineralized in the mixed layer before the next growing season (Carlson et al., 2000). Together,  $\text{Surp}(\text{TOC})/\text{NCP}$  and  $\text{Surp}(\text{DOC})/\text{NCP}$  allow us to estimate the minimum and maximum fraction NCP exported by sinking particles from the time of the summer cruise measurements to the onset of the next growing season (16 and 81%,

respectively). From NCP and Surp(TOC)/NCP (Tables 3 and 4), we estimate that  $4 \pm 3$  Tg of carbon had been exported out of the upper 100 m of the water column of the Ross Sea. Similarly, using NCP and Surp(DOC)/NCP there was a potential POC export of  $21 \pm 10$  Tg at the time that the summer cruise measurements were made for the whole Ross Sea. In a similar calculation, Nelson et al. (1996) estimated that there was 20 Tg of nitrate-based production of carbon (or new production; Eppley and Peterson, 1979) annually. Because the Ross Sea continental shelf area defined in our study is about 25% larger than that defined by Nelson et al. (1996), their estimate of new production could be as high as 25 Tg within the area outlined in this study. Thus, our potential export estimate is consistent with past studies.

## 5. Conclusion

The Ross Sea is a unique site to study the biogeochemical regimes of Antarctic continental shelves because of the consistency of the phytoplankton bloom, the diversity of regimes in a relatively small area, and the magnitude of the bloom. Based on the time-space changes in the concentrations of silica and other nutrients observed in the upper 100 m of the water column, three different regimes in the Ross Sea have been identified during the 1997 bloom period. The southwestern regime would be considered a representative site for an ice-edge bloom because of the high Def(Si)/NCP ratio of  $0.11 \pm 0.04$  (diatom dominated) and the relatively shallow mixed layer.

The regime located in the southern Ross Sea polynya had very high NCP ( $7.5 \pm 1.9 \text{ mol C m}^{-2}$ ), relatively deep mixed layers, and a low average Def(Si)/NCP ratio of  $0.04 \pm 0.02$ . The low Def(Si)/NCP ratio suggested the phytoplankton population was composed of a smaller fraction of diatoms ( $< 50\%$ ) and dominated by non-silicious species like *Phaeocystis*. The high Surp(TOC)/NCP observed during the summer cruise along the  $76^\circ 30'S$  line demonstrated that plankton in this regime do not effectively transport carbon out of the mixed layer in the early stages of the bloom, but do in the later stages when NCP is high as shown at stations near the Ross Ice Shelf. In addition, the re-occupations of stations over this region indicate that there was a substantial increase in Def(Si)/NCP, indicating that the diatom population had increasing predominance, possibly because of a gradual decrease in mixed layer depths due to surface warming.

The outer shelf regime has a much higher range of Def(Si)/NCP (0.1–0.3), indicating that this area was diatom-dominated. The relatively high Def(Si)/NCP also may be an example of a Fe-limited system (Takeda, 1998; Hutchins and Bruland, 1998) such as those observed by Martin et al. (1990) in the Ross Sea Gyre. Growth limitation by iron also may contribute to the low average NCP of  $2.6 \pm 1.0 \text{ mol C m}^{-2}$ . Alternatively, the low productivity may have been the result of prolonged ice cover (Nelson et al., 1996).

Over the whole continental shelf region of the Ross Sea, NCP was about  $25 \pm 10$  TgC between the mid-November and mid-February 1997. Although the Ross Sea remains relatively ice free until mid March (Jacobs and Comiso, 1989), primary productivity measurements made during the last stations of the summer cruise (February 8) indicate that the bloom activity was declining (Smith et al., 2000). With

senescence of the bloom we can infer a rapid decline in the daily NCP, which implies that most of the annual NCP has been observed by this study. As the season continued, much of the TOC would have been removed as particles, leaving as little as 19% (the DOC fraction) of the NCP in the upper 100 m. This leaves as much as 20 Tg of carbon potentially available to be exported to depth.

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