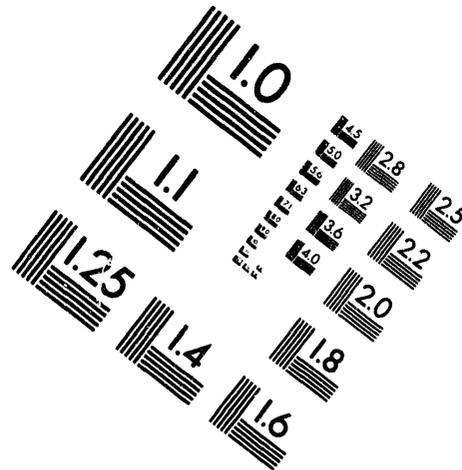
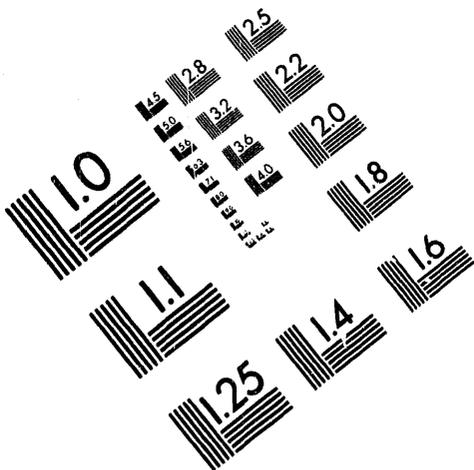




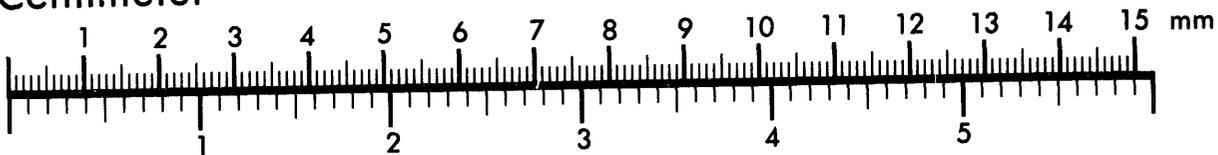
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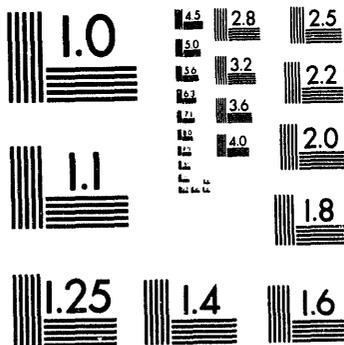
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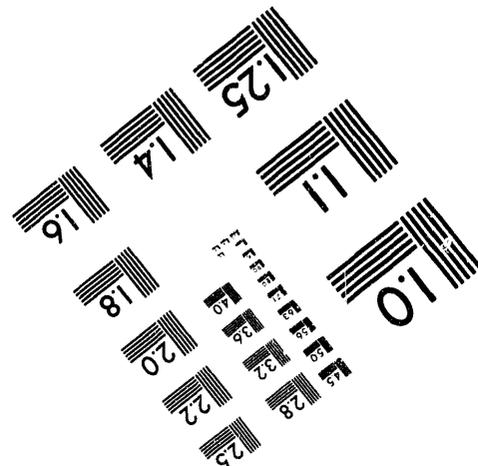
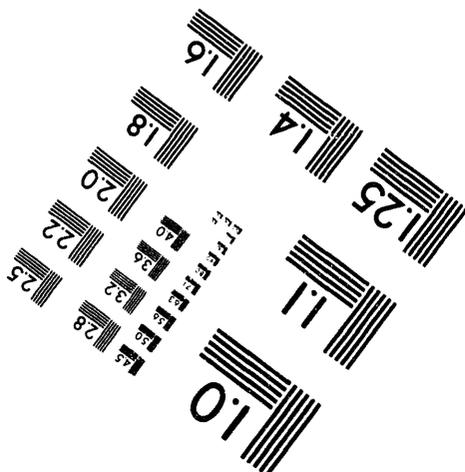
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PROGRESS REPORT
submitted to Office of Health and Environmental Research
U. S. Department of Energy
Washington, D. C. 20545
for

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Seasonal Study of Carbon Dioxide
in the Southern Extreme of the Pacific Sector,

Antarctic Ocean
to

The Trustees of Columbia University in the City of New York
Taro Takahashi, John G. Goddard, Stephany I. Rubin and Dee Breger
Lamont-Doherty Earth Observatory of Columbia University
Palisades, NY 10964

(May 5, 1994)

ABSTRACT

A 51-day oceanographic expedition in the Ross, Amundsen and Bellingshausen Seas in the Antarctic Ocean started on February 14, 1994, from McMurdo, Antarctica, and was completed successfully on April 5, 1994, at Punta Arenas, Chile. A total of 1,239 samples were analyzed for $p\text{CO}_2$, and 1,308 were analyzed for the total CO_2 concentration. In addition, the $p\text{CO}_2$ in surface water was measured continuously using an underway shower-type equilibrator and an infrared CO_2 analyzer. The preliminary data from this expedition and the observations made during previous expeditions indicate that, during the austral summer, the Pacific sector of the Antarctic Ocean south of 67°S and between 150°W and 85°W was a moderate sink for atmospheric CO_2 , with a mean sea-air $p\text{CO}_2$ difference of about -30 uatm . The eastern Bellingshausen Sea area east of about 85°W was neutral to atmospheric CO_2 , with a mean sea-air $p\text{CO}_2$ difference of about 0 uatm , whereas the Ronne Entrance area to the George VI Sound was a very strong CO_2 sink due primarily to intense photosynthesis. The total CO_2 and $p\text{CO}_2$ data indicate that there is a sharp alkalinity minimum layer at a depth of about 100 meters. The origin of this layer will be investigated in the future. The total CO_2 concentration data obtained during this expedition appear to be systematically greater by about 5 umol/kg than those from the WOCE S-4 and P-19 expeditions. This discrepancy is partially due to the use of preliminary salinity data for processing the CO_2 data. Additional sources for this discrepancy are being investigated.

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1. INTRODUCTION

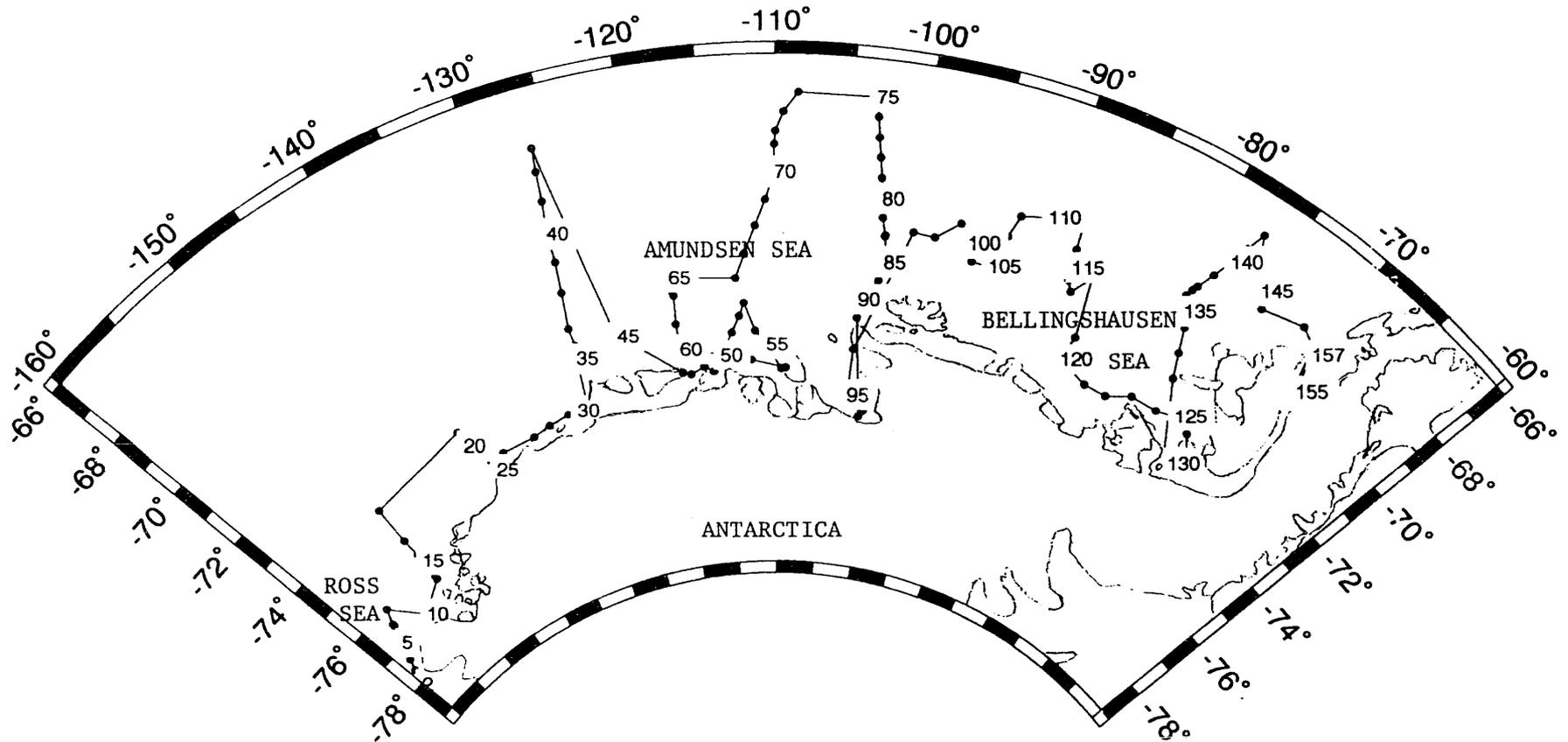
This report describes the progress made during the six-month period between December 1, 1993, when this grant was awarded, and May 1, 1994. The major aim of this investigation is to measure the distribution of the total CO₂ concentration and pCO₂ in seawater in the Pacific sector of the extreme Southern Ocean as far south as 78°S. The areas investigated include the continental shelf areas in the Ross, Amundsen and Bellingshausen Seas and the off-shore deep water areas as far north as 67°S. The measurements were made aboard the R/VIB NATHANIEL B. PALMER between February 14, 1994 and April 5, 1994, and the preliminary results are briefly described in this report. This expedition constitutes the first of a pair expeditions. The first is designed to investigate oceanic CO₂ sink/source conditions during the austral summer. The second expedition, which is designed for the following winter, has been scheduled for September, 1994.

2. DESCRIPTION OF THE SUMMER EXPEDITION, FEBRUARY-APRIL, 1994

The expedition started at McMurdo Station, Ross Island, Antarctica, on February 14, 1994, and was completed on April 5, 1994, at Punta Arenas, Chile. The ship's tracks and station locations are shown in Fig. 1. During the 51 days at sea, the total CO₂ concentration, pCO₂ in seawater and marine air were measured by John G. Goddard (party chief), Stephany I. Rubin and Dee Breger. The total CO₂ concentration and pCO₂ in discrete seawater samples were measured using a coulometer (Chipman et al., 1993) and gas chromatograph (Chipman et al., 1993) respectively. The pCO₂ measurements were made at 4.0°C. In addition, surface water pCO₂ was determined continuously using a shower-type equilibrator and infrared CO₂ analyzer (Broecker and Takahashi, 1966). A total of 1,644 discrete water samples were collected in 10-liter Niskin sampling bottles at 154 stations during the expedition at varying depths ranging from the sea surface to the sea floor. Out of these, 1,239 samples were analyzed for pCO₂ and 1,308 were analyzed for the total CO₂ concentration. Since the pCO₂ measurements were made in duplicates and the coulometer for total CO₂ measurements were calibrated often using a gas pipette and tested using Standard Reference Solutions, the actual number of analyses made at sea doubles the number of samples for each of the properties. A total of 312 measurements was made for 74 Standard Reference Solutions (Batch #18 with a total CO₂ concentration of 2115.09 ± 1.09 μmol/kg (N=7)) provided by Andrew Dickson of Scripps Institution of Oceanography. The underway pCO₂ system was successfully operated for nearly 80% of time at sea. Whenever the ship's water in-take was blocked by ice fragments, the underway pCO₂ measurement had to be discontinued.

N. Palmer 94-02 CTD-Stations

Fig. 1 Station locations occuded during the N. B. PALMER Leg 94-02 in February through April, 1994.



At 35 stations where the CO₂ properties in seawater were measured, particulate carbon samples were also collected by filtration by Andrew McTaggart. These samples will be used by John Hayes and his colleagues of Indiana University to investigate the relationships between the CO₂ concentration in seawater and ¹³C/¹²C ratios in specific organic compounds produced by photosynthesis.

3. OCEANOGRAPHIC CONDITIONS

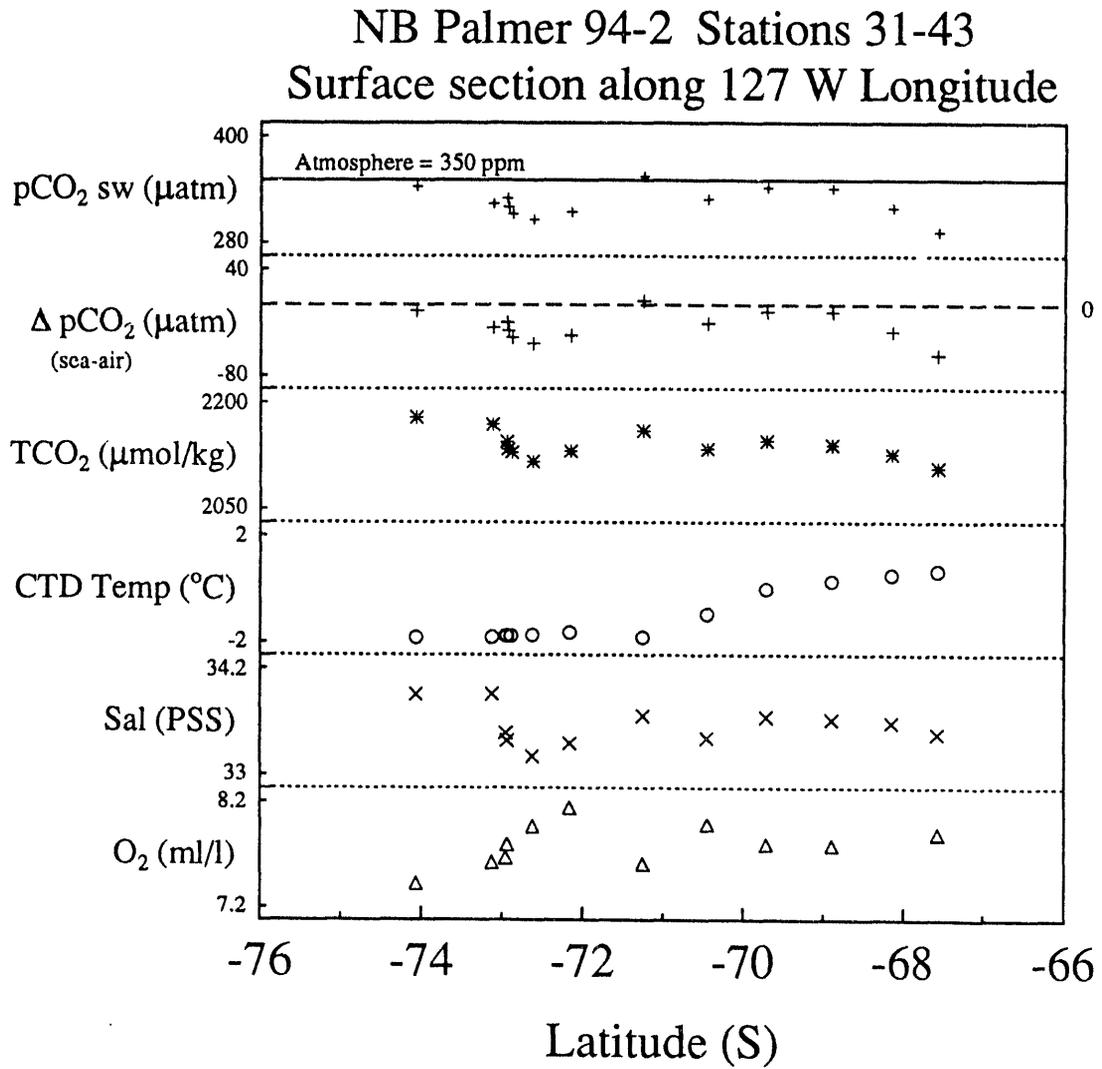
It is of interest to know general oceanographic and ice conditions in the southern extreme of the Pacific Ocean during the expedition. The following is reproduced from the Chief Scientist's Cruise Report for NBP94-02 prepared by Stanley S. Jacobs (1994).

"Both the sea and glacial ices are extraordinary in the Amundsen and Bellingshause Seas, with a wide diversity in new sea ice forms and old iceberg shapes. Heterogeneous mixtures of old and new ice floes were very common, along with ample evidence of snow ice formation. Most floes thicker than 15 cm were rotten at the base, in part because of the late-summer season. However, the warm water on the shelf must effectively limit sea ice growth from below, particularly in areas where this water shoals due to offshore winds. In addition to this, the absence of newly-formed shelf water also implies a strong and perhaps dominant sensible heat component in the coastal polynyas."

"Nowhere else have we seen so many icebergs, and they were often grounded and surrounded by close or fast ice. This grounding, in combination with prevailing light easterly and northerly winds, must contribute to a generally sluggish ocean circulation on the continental shelf. It may also play a role in the maintenance of some of the open water along the coastline, in particular the Amundsen Polynya. Several CTD casts were made during a circumnavigation of the world's oldest and largest iceberg, B-10, which is grounded on the floor of the Amundsen shelf. Most of its perimeter appears to be afloat, and at these locations the basal melting must be of the order of a few meters per year. However, the high surface accumulation rate in this sector may help to keep many of the bergs well-grounded on the shelf, leading to a lengthy residence time."

"One feature that is not well-developed in this region is the Antarctic Slope Front. Indications of a weak front were encountered at some slope crossings, but nothing compare with the strong fronts in the Ross and Weddell Seas. We did observe evidence of upwelling north of the shelf, where the surface layers are substantially thinner than over the slope and shelf. Most of the

Fig. 2 Meridional distribution of surface water properties along 127°W, March, 1994, in the western Amundsen Sea area.



deep water columns were unremarkable, with only minor boundary layers and little thermohaline evidence of recent renewal near bottom."

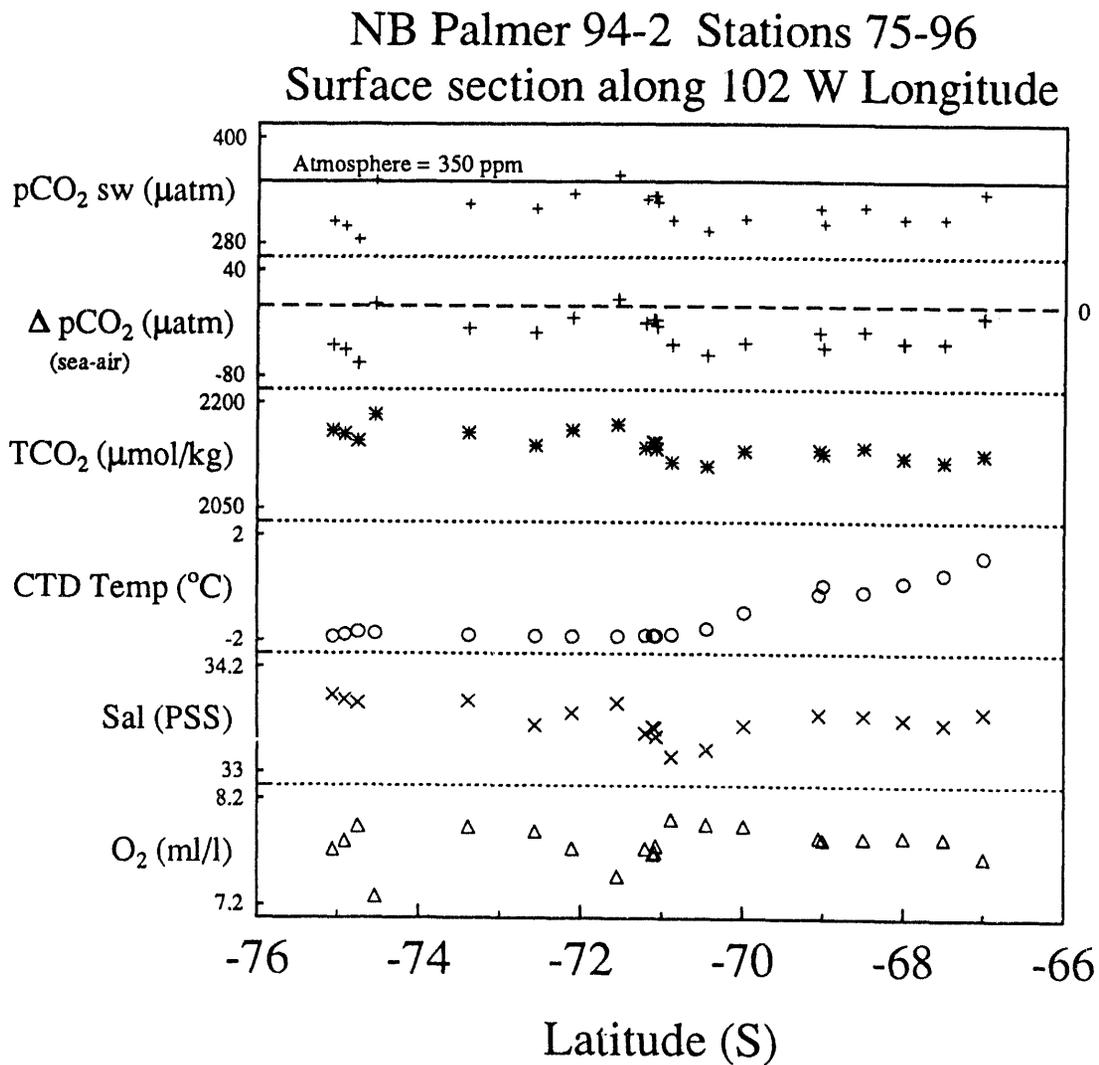
4. CO₂ SINK/SOURCE CONDITIONS IN SURFACE WATERS

Fig. 2 shows the meridional distribution of six surface water properties observed at Stations 31 through 43 (see Fig. 1) located along 127°W in the Amundsen Sea. Station 31, the southernmost station in this section, is located within the Wrigley Gulf off the Getz Ice Shelf, and Station 43, the northernmost station, is located at about 67.5°S. The surface water temperature was near the freezing point of -1.9°C in near shore waters and off-shore waters as far north as 71°S, and increased northward to about 1°C at 67.5°S. While these cold waters had greater total CO₂ concentrations, they had much lower oxygen concentrations especially south of 72°S, suggesting the presence of upwelled deep waters or the effect of the oxidation of organic matter over the shelf area. Surface waters along this section were either saturated or undersaturated locally by as much as -60 uatm with respect to atmospheric CO₂, and hence this area was a moderate CO₂ sink on the average.

Fig. 3 shows the meridional distribution of the same surface water properties observed at Stations 75 through 96 (see Fig. 1) located further east along 102°W in the easternmost Amundsen Sea. Stations 90 through 96 are located south of 72°S in Pine Island Bay or close to the shore on the Amundsen Sea shelf. While the surface waters located on the shelf had colder temperatures close to the freezing point of seawater, they exhibited greater total CO₂ concentrations and lower oxygen concentrations than those observed in the off-shore waters. These features suggest again the presence of upwelled deep waters or the effects of the oxidation of organic matter in shelf sediments. The surface waters along this section were mostly undersaturated with respect to atmospheric CO₂ by about -30 uatm (10%) on the average, and hence were moderate CO₂ sinks.

The results obtained along these two meridional sections suggest that the surface ocean was a moderate sink for atmospheric CO₂. The results obtained in April, 1992 along the WOCE S-4 section also indicate that, with the exception of three narrow bands, the oceanic area along 67°S between 100°W and 170°E was also a moderate CO₂ sink with a mean sea-air pCO₂ difference of about -30 uatm. These observations together suggest that the Amundsen Sea area south of 67°S to the edge of the Antarctica continent (about 75°S) was a moderate CO₂ sink during the austral summer months.

Fig. 3 Meridional distribution of surface water properties along 102°W, March, 1994, in the eastern Amundsen Sea area.



The distribution of surface properties further east near the Antarctic Peninsula was found to be significantly different from those along the 102°W and 127°W sections. Fig. 4 shows the distribution of surface water properties observed along the longitudes between 70°W and 80°W at Stations 124 through 142 (see Fig. 1). Near the Ronne Entrance area located between 71°S and 72°S in the southeastern corner of the Bellingshausen Sea, the total CO₂ concentration, pCO₂ and salinity were dramatically lower, while the oxygen concentrations were higher and temperature was near freezing. Sea-air pCO₂ differences as low as -160 uatm (or 50% undersaturation) were observed. Total CO₂ concentrations were as much as 110 umol/kg lower than the mean open ocean value of 2160 umol/kg. These features may be attributed to intense photosynthesis occurring in the confined entrance area water of the George VI Sound. North of 72°S, the total CO₂ concentration increased rapidly to the mean open ocean value, and surface waters were nearly saturated with atmospheric CO₂ to as far north as 67°S. Our March-1992 data obtained along 67°S show also that surface waters were nearly saturated with atmospheric CO₂ between 72°W and 86°W. These observations suggest that the Bellingshausen Sea area west of the Antarctic Peninsula was neutral to atmospheric CO₂, whereas the George IV Sound was a very strong CO₂ sink during the austral summer.

5. DISTRIBUTION OF CO₂ IN DEEP WATERS

The locations of two stations occupied during the present expedition coincided closely with those occupied during the WOCE S-4 expedition (aboard the Russian Research Ship IOFFE) in March, 1992 and the WOCE P-19 expedition (aboard the R/V KNORR) in January, 1993. The results of the total CO₂ and pCO₂ measurements made during these expeditions are compared in Figs. 5 and 6. All the pCO₂ values shown represent the values at 4.0°C, at which the measurements were made.

The total CO₂ concentrations and pCO₂ values obtained at Station 74 of this expedition are compared in Fig. 5 with those determined at Station 715 of the IOFFE (S-4) expedition, both located at 67.00°S and 108°30'W. Below about 500 meters, while the pCO₂ values for these two stations agree within experimental uncertainties, the total CO₂ values for this expedition are on the average 4 umol/kg systematically greater than those for the IOFFE station. This discrepancy can be attributed partially to the preliminary salinity values used for computing the density of seawater, which was used to convert "per liter" concentration to "per kg" concentration. The discrepancy may

Fig. 4 Meridional distribution of surface water properties along 75°W, March-April, 1994, in the eastern Bellingshausen Sea.

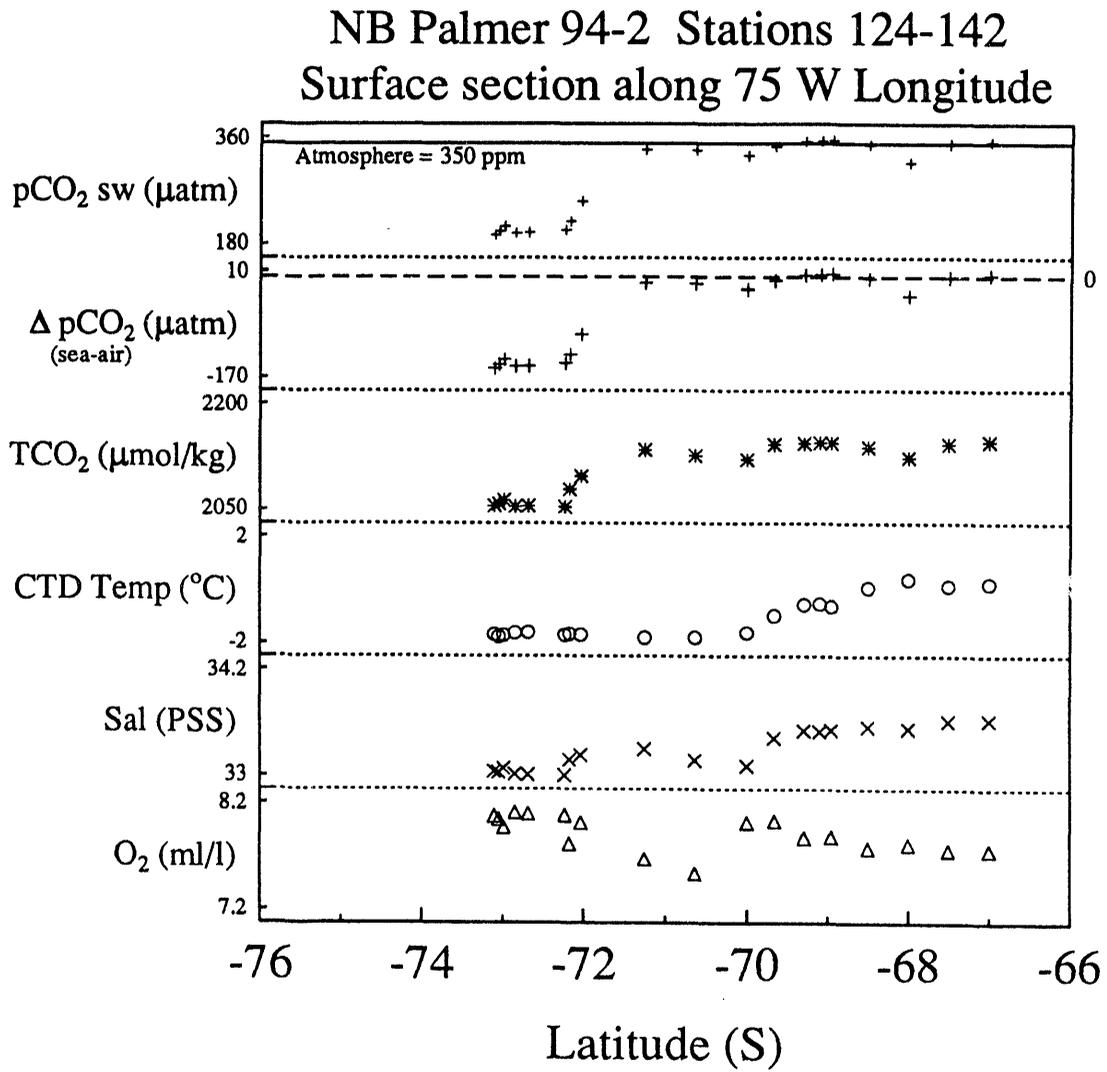


Fig. 5 Vertical profiles of the total CO_2 concentration and pCO_2 observed at 67.00°S and $108^\circ30'\text{W}$ during the PALMER and IOFFE expeditions in March, 1994 and March, 1992, respectively.

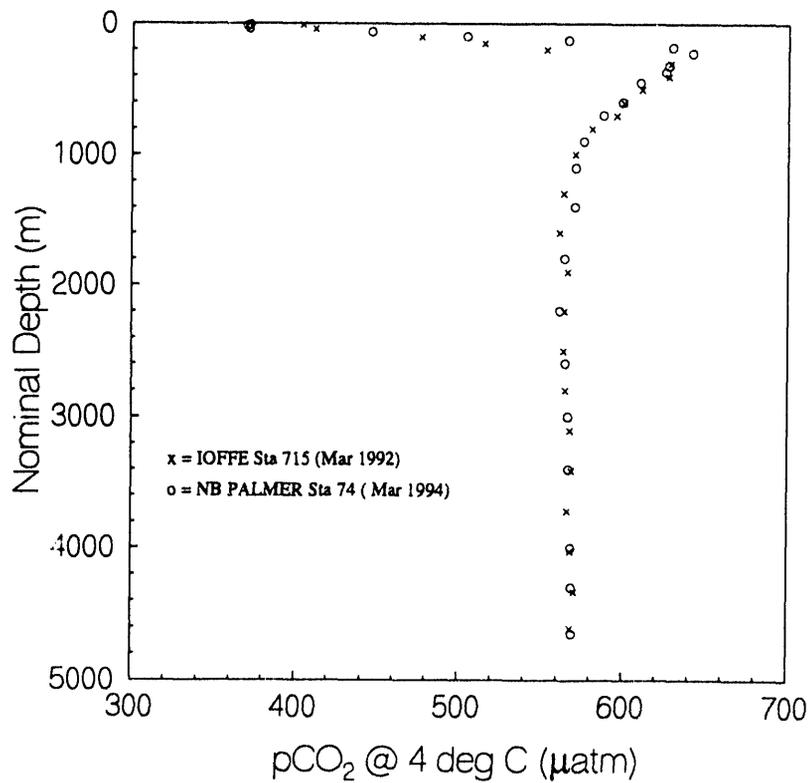
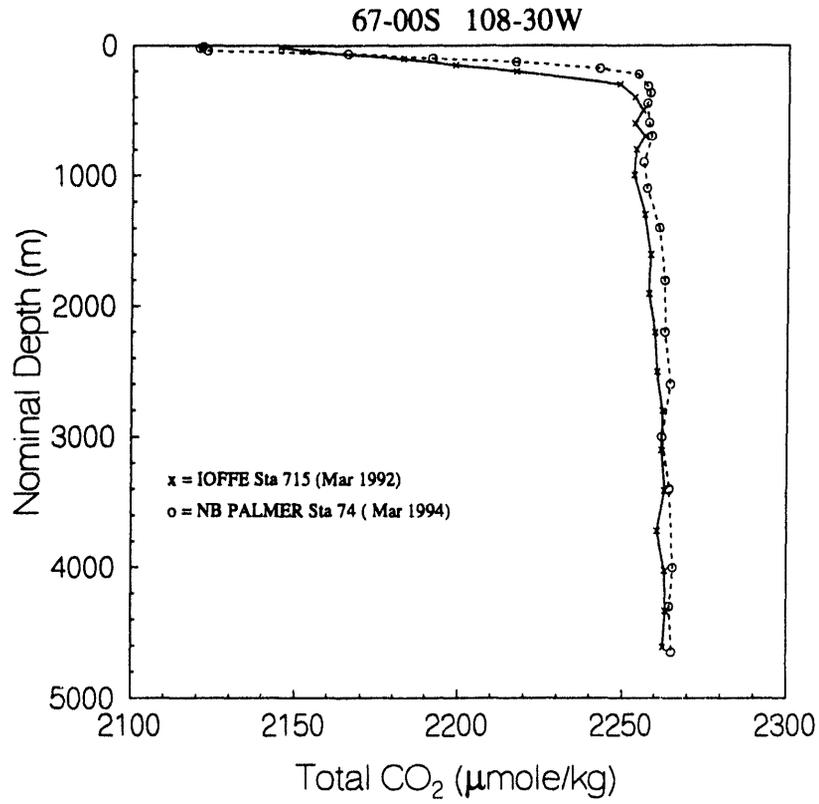
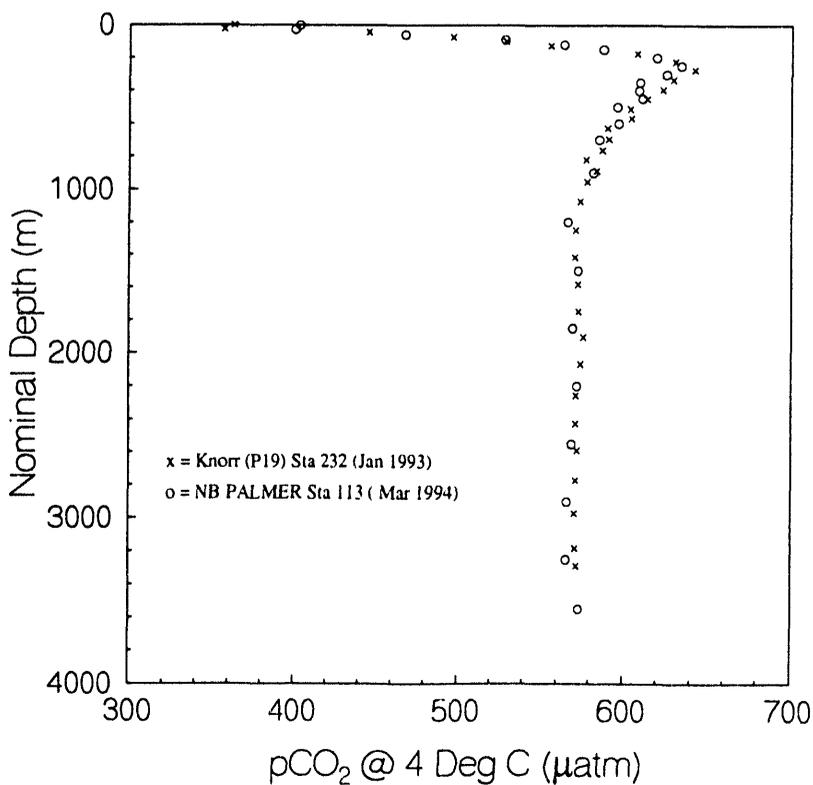
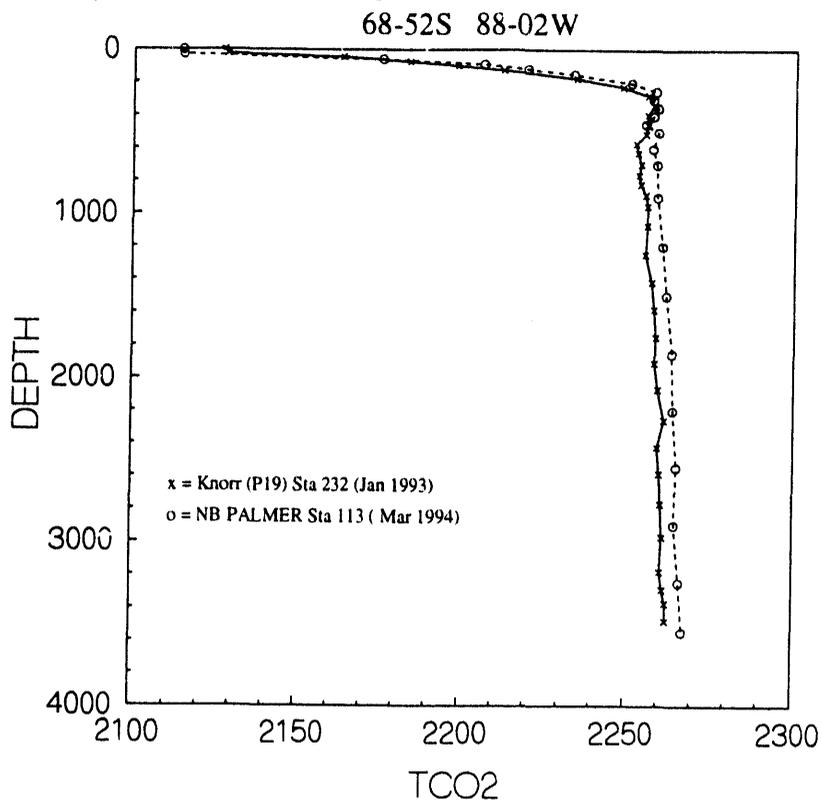


Fig. 6 Vertical profiles of the total CO₂ concentration and pCO₂ observed at 68°52'S and 88°02'W during the PALMER expedition in March 1994, and the KNORR expedition in January, 1993.



also have been caused by changes in the volume and/or temperature of the calibration gas loops. We are currently investigating possible sources for the discrepancy.

In the depths shallower than 500 meters, the total CO₂ and pCO₂ values for this expedition were both greater than those observed during the IOFFE expedition in 1992. In this depth range, the salinity values for this expedition were also found to be systematically greater by as much as 0.3 PSS compared to those for the IOFFE expedition (Jacobs, 1994). Thus, the changes observed for the CO₂ properties are real.

Fig. 5 shows that there is a sharp pCO₂ maximum at depth of about 100 meters. Since this was not accompanied with a maximum in the total CO₂ concentration, this may be attributed to an alkalinity minimum at this depth. Whether this alkalinity minimum is due to CaCO₃ production at the base of winter sea ice or to unique biogeochemical processes occurring in shelf waters is not understood at this stage. These features will be investigated in the future.

In Fig. 6, the results obtained at Station 113 of the present expedition are compared with those obtained at Station 232 of the WOCE P-19 expedition in January, 1993, both located at 68°52'S and 88°02'W. As seen in Fig. 5, the total CO₂ concentrations for this expedition were on the average 5 umol/kg greater than those for the P-19 expedition. This discrepancy may be attributed to the preliminary salinity data used for our data processing and/or to errors in calibration. The sources for this discrepancy will be further investigated. The pCO₂ data from these two expeditions agree within the scatter of the data.

Similar to Station 74, a sharply defined pCO₂ maximum was observed at a depth of 100 meters, indicating an alkalinity minimum. Thus, this feature appears to be wide spread over the southern extreme of the South Pacific Ocean.

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