

PROGRESS REPORT

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Measurements of the total CO₂ concentration
and partial pressure of CO₂ in seawater
during WOCE expeditions in the South Pacific Ocean

by

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ABSTRACT

During the first year of the grant, No. DEFG02-93ER61539, we participated in three WOCE expeditions (a total of 152 days at sea) in the South Pacific Ocean, and the field phase of the proposed investigation has been successfully completed. The total CO₂ concentration and pCO₂ were determined at sea in 4,419 water samples collected at 422 stations. On the basis of the shipboard analyses of SIO Reference Solutions for CO₂ and a comparison with the results of previous expeditions, the overall precision of our total CO₂ determinations is estimated to be about ± 2 $\mu\text{M}/\text{kg}$. The deep water data indicate that there is a CO₂ maximum centered about 2600 meters deep. This appears to represent a southward return flow from the North Pacific. The magnitude and distribution of the CO₂ maximum observed along the 135.0°W meridian differ from those observed along the 150.5°W meridian due to Tuamotu Archipelago, a topographic high which interferes with the southward return flow. The surface water pCO₂ data indicate that the South Pacific sub-tropical gyre water located between about 15°S and 50°S is a sink for atmospheric CO₂.

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INTRODUCTION

This report covers the period, September 1, 1992 through June 30, 1993, which represents the first year of the investigation supported by DOE grant, No. DEFG02-93ER61539. According to the original proposal, the first year was designated for field measurements of CO₂ during three WOCE expeditions in the South Pacific Ocean. We have completed the field phase as scheduled, and our preliminary data processed to-date are presented. Our work is progressing on schedule, and the remaining data are being processed and analyzed.

FIELD OPERATIONS

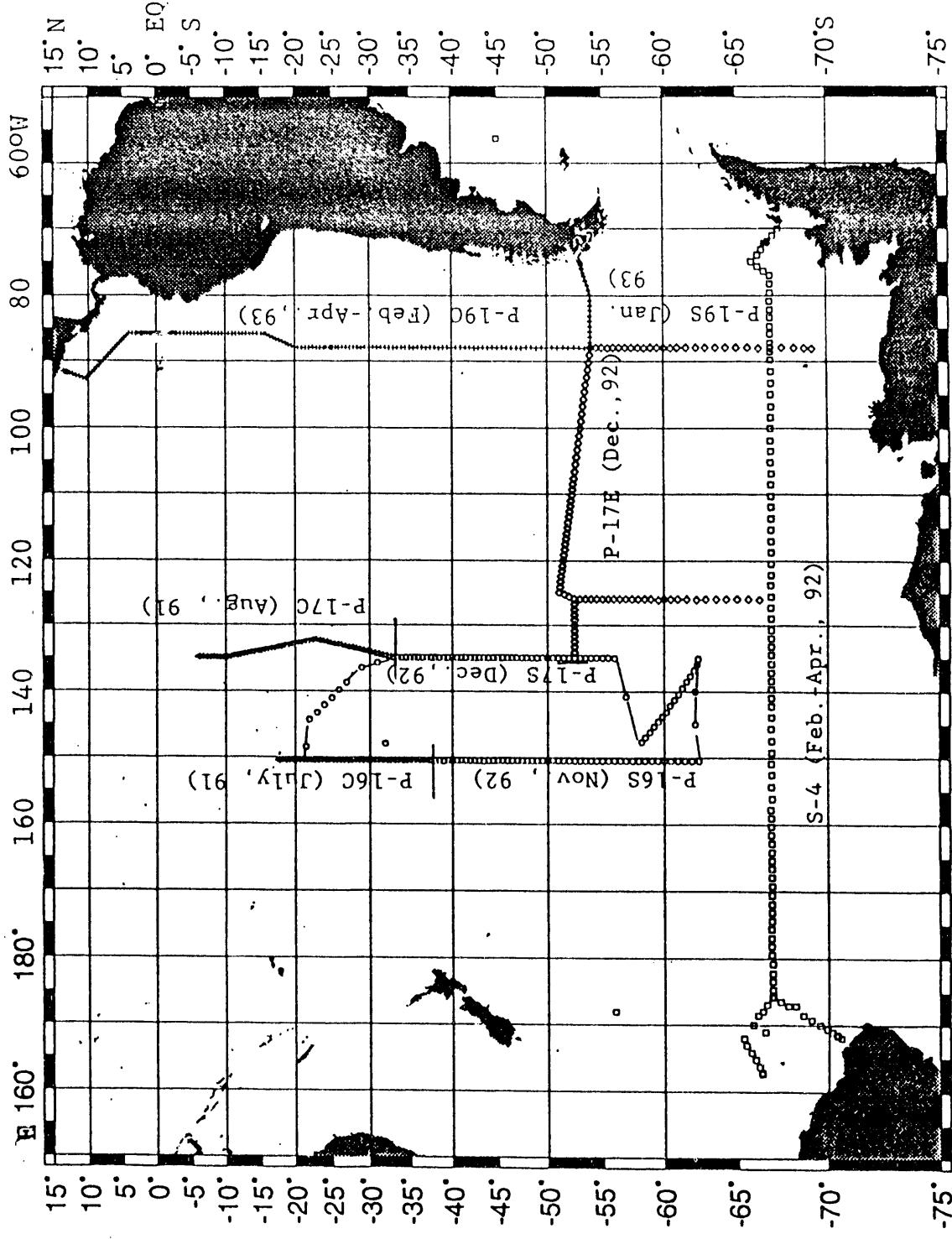
Ocean water samples were collected during the three WOCE expeditions, a total of 152 days at sea, aboard the R/V Knorr. Fig. 1 shows the station locations where measurements were made during the investigation. Station locations occupied during other WOCE expeditions, for which we have completed CO₂ measurements during previous years, are also shown to illustrate how the present measurements are located with respect to those completed during previous investigations. Table 1 shows the WOCE leg designations, ports of call, dates of the expeditions, and number of hydrographic stations occupied. The number of stations where CO₂ properties were measured from the sea surface to the ocean floor are shown in parentheses.

Table 1 - Schedule of the Field Operations

WOCE Exped. Hydrographic Designations	Ports of Call	Dates	No. of Stations
P-16S/P-17S	Papeete, Tahiti Papeete, Tahiti	Oct. 6, 92 Nov. 25, 92	127 (39)*
P-17E/P-19S	Papeete, Tahiti Punta Arenas, Chile	Dec. 4, 92 Jan. 22, 93	106 (31)*
P-19C	Punta Arenas, Chile Panama City, Panama	Feb. 22, 93 Apr. 13, 93	189 (44)*
Total 152 days at sea			422 (114)*

*/ The values in parentheses indicate the numbers of stations where CO₂ measurements were made normally at 36 levels from the surface to the ocean floor. The CO₂ measurements were made only in the surface mixed layer at all other stations.

Fig. 1 - Station locations for the three WOCE Expeditions during which the CO_2 measurements were made for the present investigation. Stations for the earlier expeditions during which we made measurements are also indicated.



DETERMINATION OF CO₂ IN SEAWATER

Procedures:

The total CO₂ concentration and pCO₂ in seawater samples were determined using a coulometer system and an equilibrator/gas chromatograph system respectively. The methods used are described by Chipman et al. (1992). Samples for total CO₂ determinations were collected from Niskin water samplers in 500 ml Pyrex bottles with ground glass stoppers and those for pCO₂ determinations in 500 ml long-neck volumetric flasks with small screw tops. To minimize biological activity during the storage of samples prior to analyses, 0.20 ml of 50%-saturated mercuric chloride solution was added to each bottle. These samples were stored in darkness at room temperature before their analyses which were made generally within 24 hours after sampling. The total number of water samples analyzed and number of analyses performed during each of the expeditions are summarized in Table 2. During the 152 days at sea, the total CO₂ concentration and pCO₂ have been determined on a total of 4,419 water samples.

Table 2 - Summary of CO₂ Determinations Made at Sea

Expedition Designations	No. of Days at Sea	No. of Seawater Samples	Total Number of Analyses
P-16S/P-17S	51 days	TCO ₂ 1,549 pCO ₂ 1,549	~1,700 ~4,700
P-17E/P-19S	50 days	TCO ₂ 1,282 pCO ₂ 1,280	~1,440 ~3,900
P-19C	51 days	TCO ₂ 1,588 pCO ₂ 1,590	~1,850 ~4,800
<hr/> TOTAL	152 days	TCO ₂ 4,419 pCO ₂ 4,419	~4,990 ~13,400

Calibration of the Coulometer:

The coulometer system used for total CO₂ determinations was calibrated several times a day by injecting it with a known number of moles of pure CO₂ gas (99.9995%). The amount of CO₂ gas was determined based upon the volume of a precision gas pipette, and the pressure and temperature of gas in it, as described by Chipman et al. (1992). The

performance of the coulometer was evaluated by comparing the reference values for SIO Reference Solutions (provided by Andrew Dickson) with those obtained for the Solutions using our coulometer at sea. The reference values were determined in the laboratories of C. D. Keeling of SIO using his manometric method. The results of measurements are summarized in Table 3. Figs. 2-A through 2-C show the results of the analyses as a function of the Julian date in 1992.

Table 3 - Results of Analyses for the SIO Reference Solutions

Expedition	No. of SRM Bottles	No. of Analyses	Mean CO ₂ Conc. (uM/kg)	Reference Conc. (uM/kg)	Difference (uM/kg)
P-16S/P-17A	73 (Batch #12)	311	1983.8±1.9	1984.3±0.7 (N = 7)	-0.5
P-17E/P-19S	90 (Batch #13)	266	2013.7±2.1	2014.9±0.3 (N = 5)	-1.2
P-19C	97 (Batch #13)	386	2015.1±1.8	2014.9±0.3 (N = 5)	+0.2
TOTAL	260	963			

The table and figures show that the precision of our measurements made at sea is on average about ±2.0 uM/kg as expressed in terms of one standard deviation for a single analysis, and that the mean of our measurements agree with the reference values within one standard deviation. Causes for a shift of about 1.4 uM/kg in the mean ship board values for the second and third expeditions are not clear and are being investigated.

PRELIMINARY RESULTS

Deep Ocean Regime:

To date, the measurements of total CO₂ concentration in seawater made during the first of the three expeditions have been processed. It is instructive to learn how the results of this expedition agree with those of the previous expeditions. In Fig. 3-A, the total CO₂ data which were obtained on August 12, 1991 at the southern most station (Stn. 180) of the WOCE P-16C Expedition located at 37.5°S and 150.5°W are compared with those obtained about one year later on October 12, 1992, at Stn. 3 of this expedition located at the same position. Although differences as large as 5 uM/kg are observed between these sets of measurements at some depths (see

Fig. 2 - The coulometric total CO_2 determinations of the SIO Reference Solutions (Batches 12 and 13) performed during the three WOCE Expeditions. A total of 963 measurements were made during 152 days at sea. The solid lines indicate the mean value for each leg; the dotted lines, one standard deviation; and the chain lines, the reference values based upon the manometric measurements by C. D. Keeling.

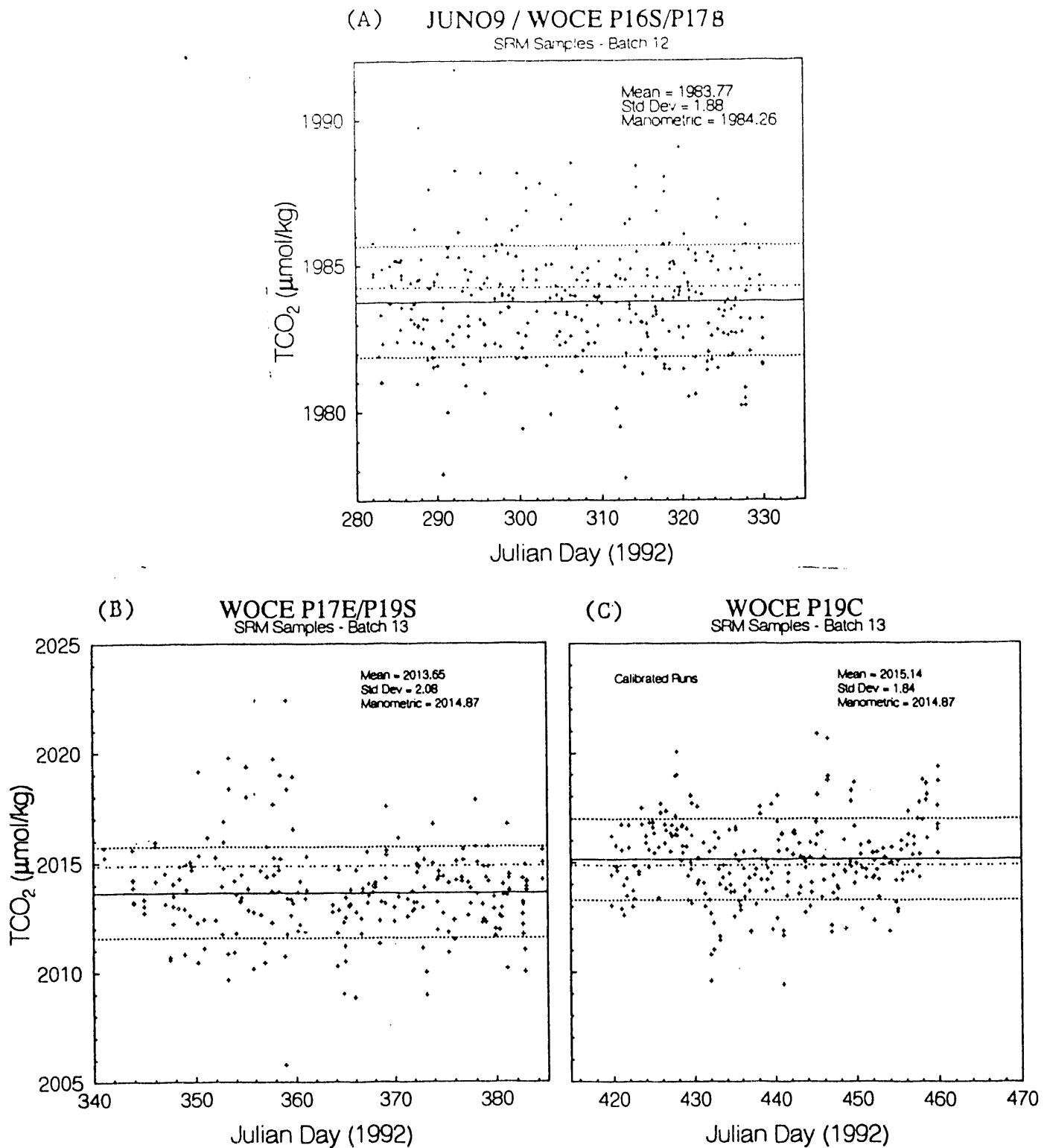


Fig. 3 - Comparison of the total CO_2 data obtained during the P-16C/17C WOCE Expeditions in 1991 with those obtained during the present expedition in 1992. A) at 37.5°S and 150.5°W ; and B) at 33.0°S and 135.0°W . On the average, the results of the earlier expeditions are consistent with those of the present expeditions within 2 $\mu\text{M}/\text{kg}$.

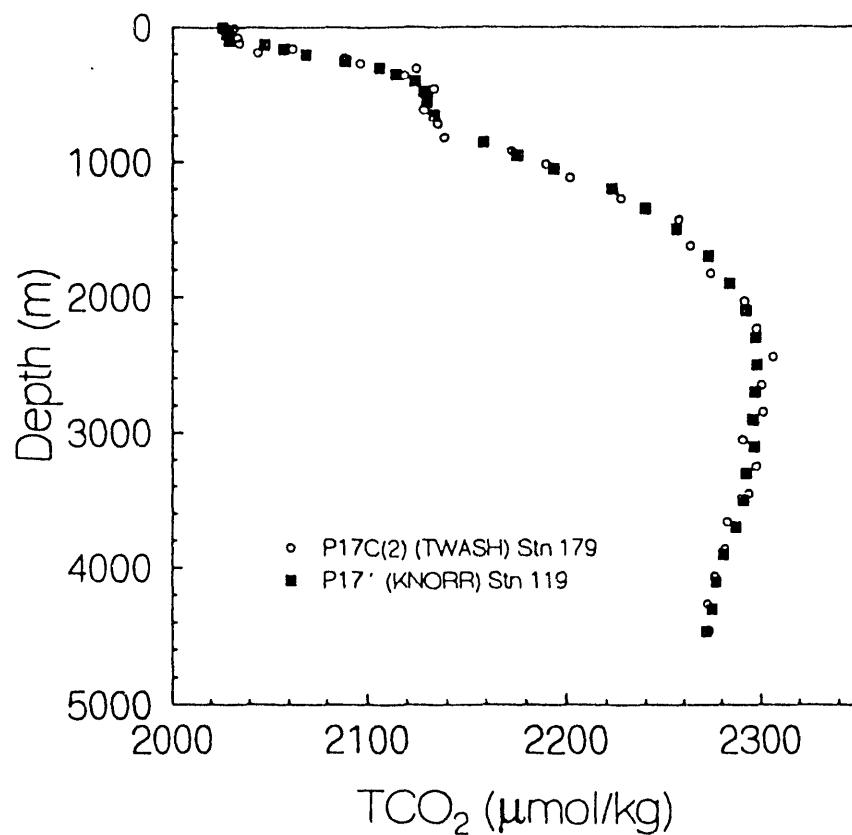
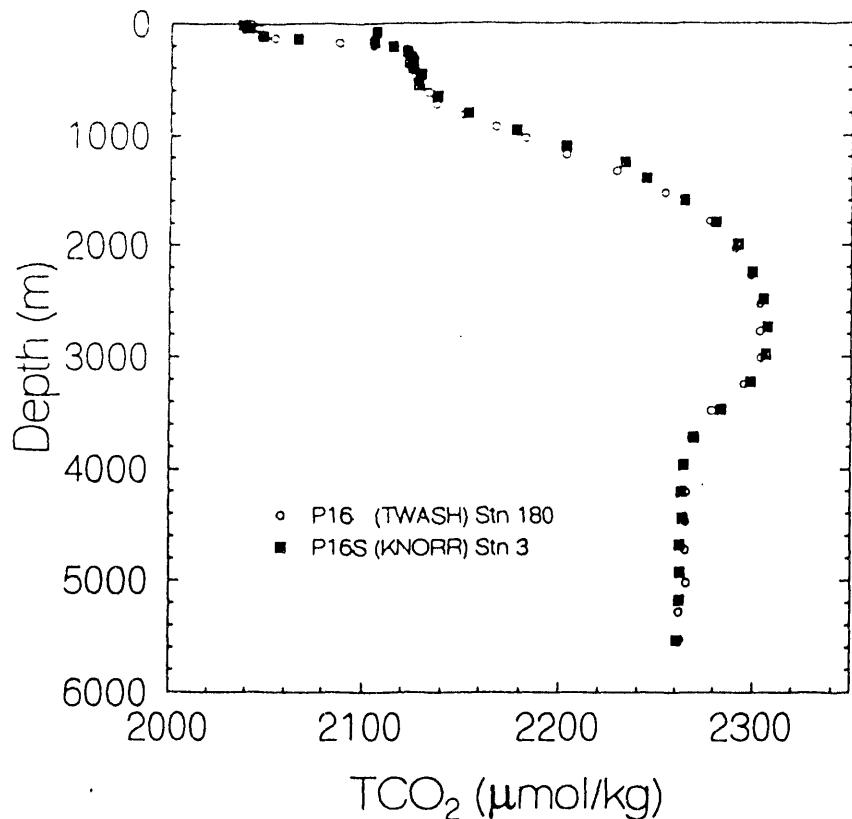


Fig. 4 - A meridional section for the total CO_2 concentration in seawater along the WOCE Section P17, 135.0°W . The results south of 33°S represent those obtained during the present investigation, and those north of it were obtained during our previous investigation in 1991.

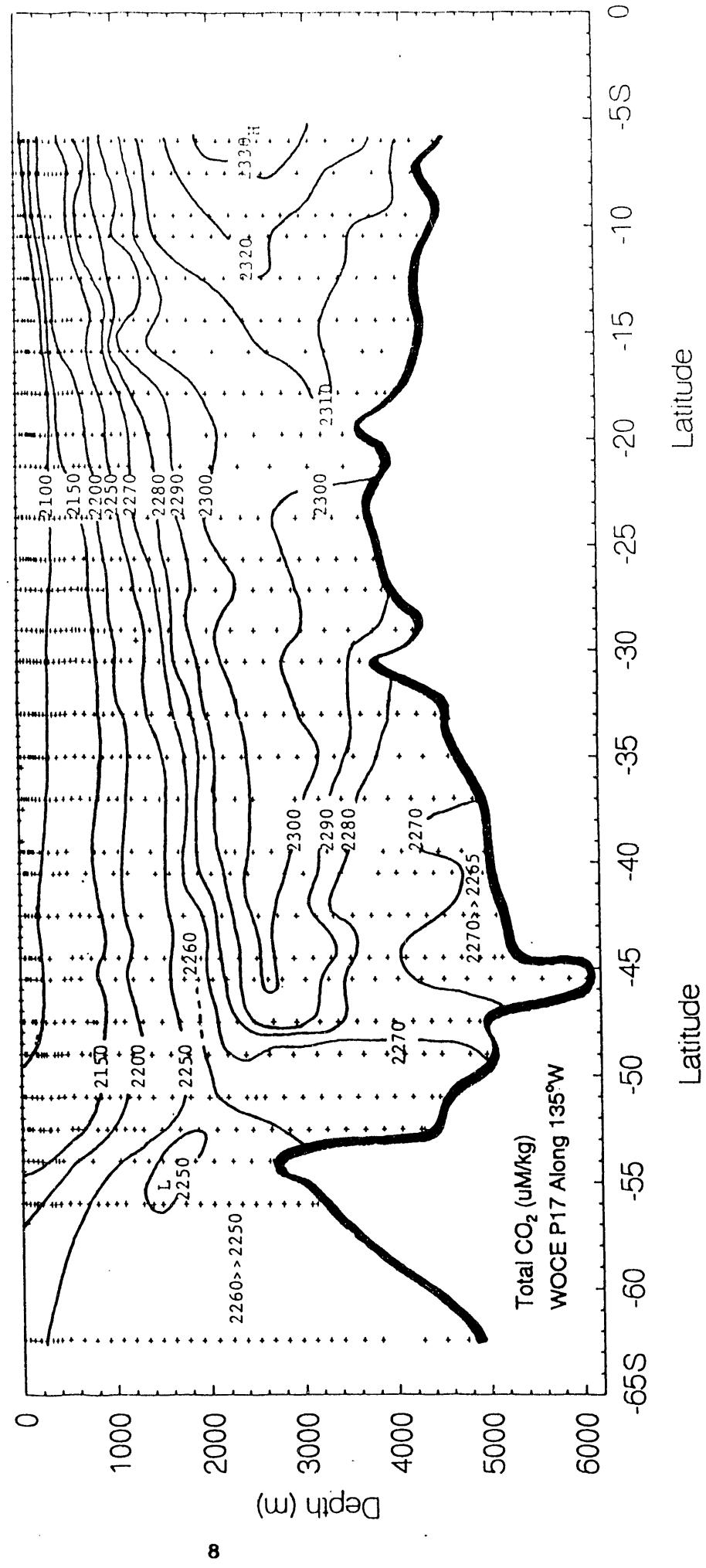
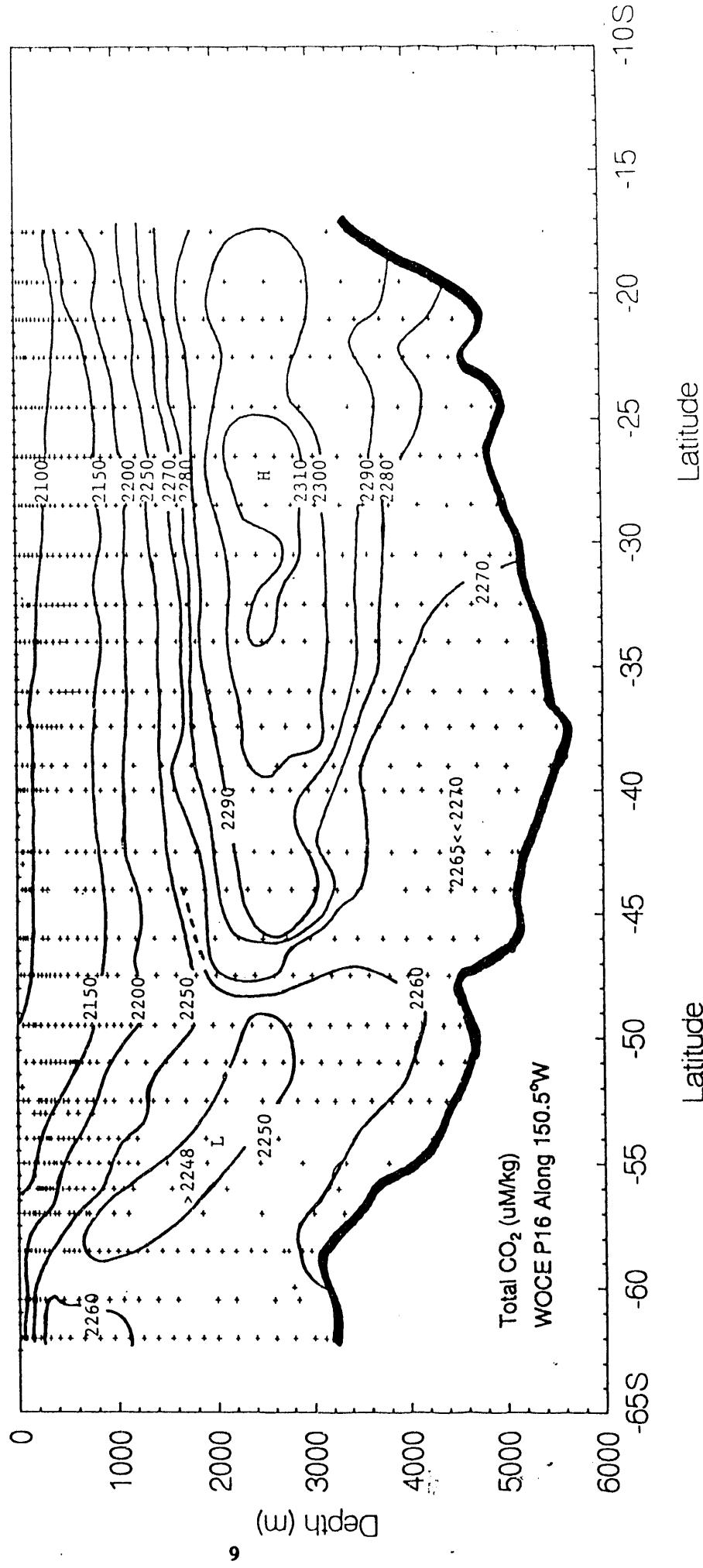


Fig. 5 - A meridional section for the total CO_2 concentration in seawater along the WOCE Section P-16, 150.5°W. The results south of 37°S represent those obtained during the present investigation, and those north of it were obtained during our previous investigation in 1991.



points at about 1300, 2800 and 5100 meters in Fig. 3-A), the mean difference between them is less than 2 $\mu\text{M}/\text{kg}$. Fig. 3-B also shows a comparison between the data set obtained on August 8, 1991, at Station 179 of the WOCE P-17C expedition and that obtained on November 20, 1992, at Station 119 of this expedition at about 33°S and 135°W . The magnitude of differences between them is similar to that observed at the previous pair of stations. Therefore, on the bases of these observations and the consistency with the SIO Reference Solutions, we estimate that our total CO_2 data are precise to and coherent within $\pm 2 \mu\text{M}/\text{kg}$.

Meridional distributions of total CO_2 concentration along 135.0°W (P-17) and 150.5°W (P-16) in the South Pacific are shown in Figs. 4 and 5 respectively. In the 135.0°W section, the data north of about 33°S were obtained during our previous expedition (P-17C) in 1991 and those south of it represent the results of the present investigation. In the 150.5°W (P-16) section, the data south of about 33°S represent the results of this study.

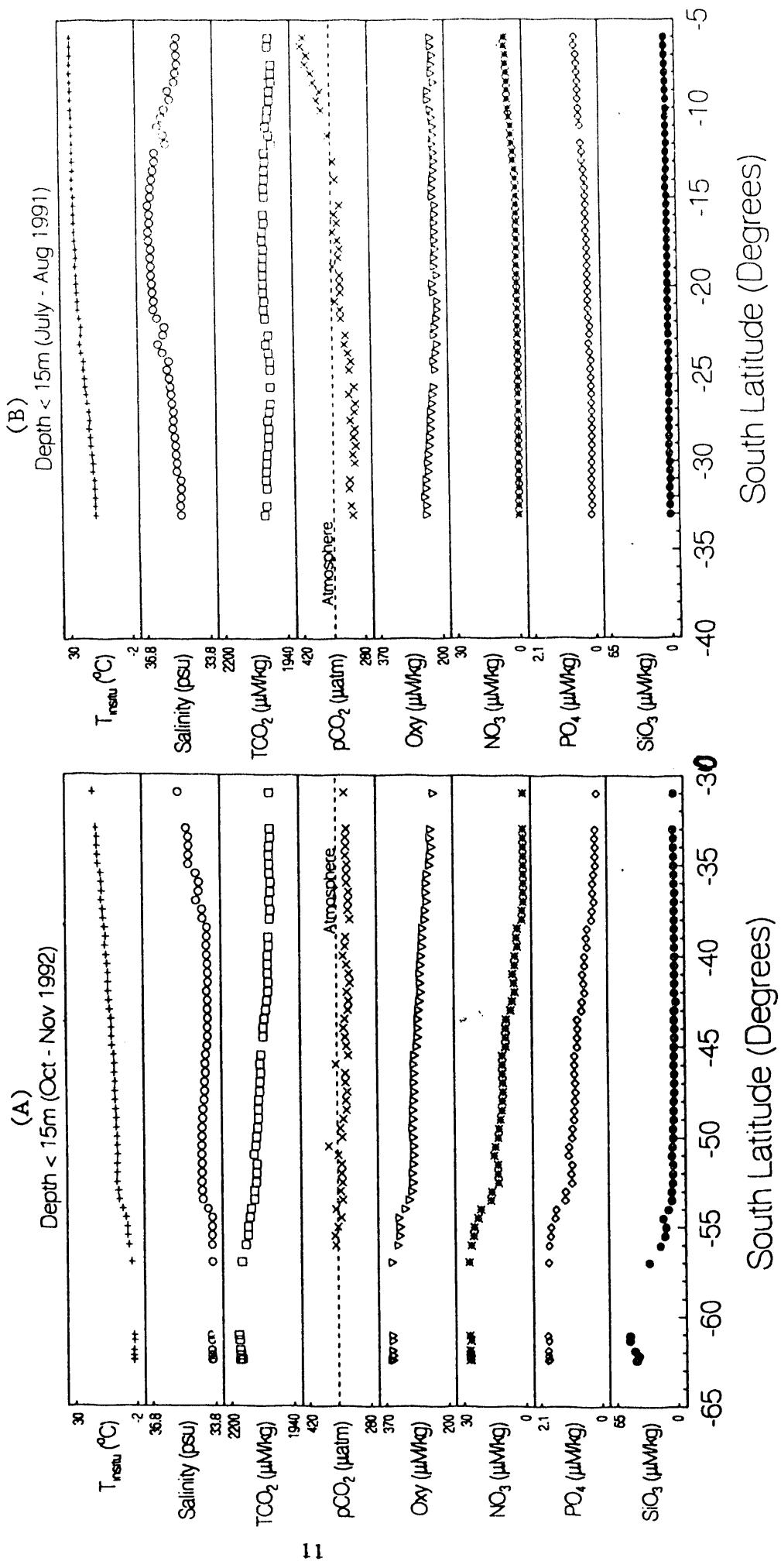
In Fig. 4, a mid-depth CO_2 maximum which is centered about 2600 meters is observed. The highest concentrations exceed $2330 \mu\text{M}/\text{kg}$ in the northern extreme (about 6°S) of the section, and decrease to about $2280 \mu\text{M}/\text{kg}$ near 48°S , where the maximum disappears. This high CO_2 tongue appears to represent the southward return-flow from the North Pacific. The mid-depth maximum is created by the northward intrusion of denser low- CO_2 Southern Ocean waters along the floor of the ocean. The CO_2 concentration in the Southern Ocean deep waters below 500 meters is nearly uniform and ranges between 2250 and $2260 \mu\text{M}/\text{kg}$.

In Fig. 5, the feature of the mid-depth CO_2 maximum is also observed. However, in this section along 150.5°W , the highest concentration is about $2310 \mu\text{M}/\text{kg}$ and smaller than those observed along the 135.0°W section. Furthermore, the 2300 and $2310 \mu\text{M}/\text{kg}$ contours are closed both to the north and south in the 150.5°W section, whereas they are open to the north in the 135.0°W section. These differences may be attributed to the presence of a large topographic high, the Tuamotu Archipelago, located 15°S - 25°S and 130°W - 150°W , which diverted the southward flow of the high CO_2 water.

Surface Waters:

Fig. 6-A shows the distribution of eight properties observed in surface waters along the 135.0°W meridian between 31°S and 63°S during the present investigation aboard the R/V Knorr in October-November, 1992. Fig. 6-B shows the same properties observed during our previous expedition in

Fig. 6 - Eight properties in the surface mixed layer along the 135.0°W meridian (WOCE P-17 section). A) Observations which were made in October-November, 1992, during the first expedition of this investigation; and B) those which were made in July-August, 1991, during the WOCE P-17C Expedition aboard the R/V Thomas Washington.



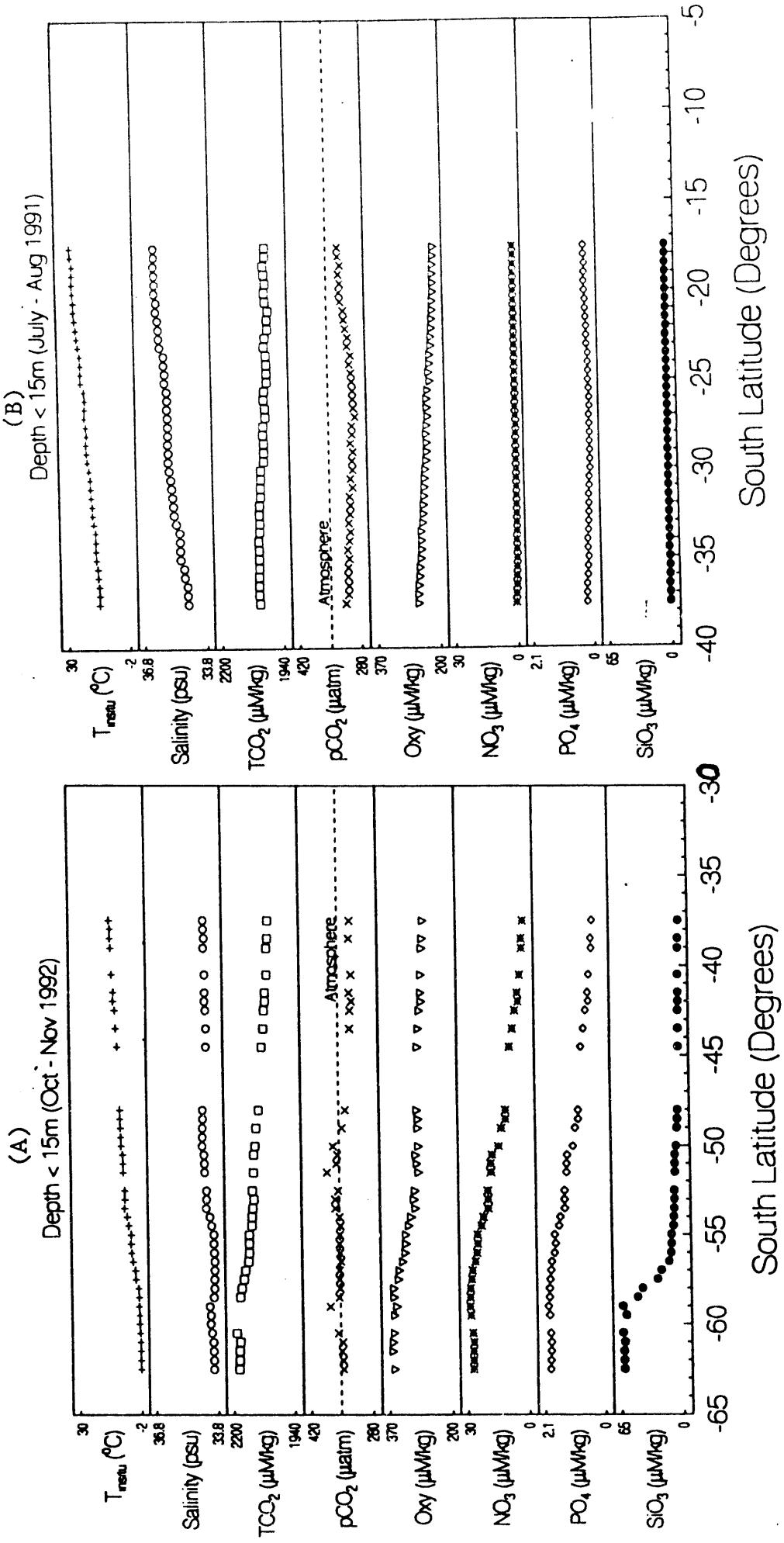
July-August, 1991, between 6°S and 33°S also along the 135.0°W meridian. In Fig. 6-A, a sudden southward decrease in temperature and salinity is observed at about 55°S. This is accompanied with a sharp southward increase in the concentrations of CO₂, oxygen and nutrients. This feature represents the Antarctic Convergence. Another sharp change is observed near 38°S, north of which the concentrations of three nutrients decreased to near zero. This feature represents the Sub-tropical Convergence. The pCO₂ data show that the surface water north of the Antarctic Convergence is a sink for atmospheric CO₂, and that this trend continues as far north as 13°S (see Fig. 6-B). The warm surface water north of this latitude is a CO₂ source due primarily to the effect of equatorial upwelling.

Fig. 7-A shows the same eight properties observed during the present investigation (October through November, 1992) in surface waters between 37°S and 63°S along 150.5°W, and Fig. 7-B shows those observed during the previous expedition in July-August, 1991, also along 150.5°W. While the surface water temperature and salinity decrease from north to south, all other properties including the total CO₂ concentration, pCO₂ and the concentrations of dissolved oxygen, nitrate, phosphate and silica increase from north to south. The changes in properties associated with the Antarctic Convergence are less sharp in this section than the 135°W section. The nitrate concentration is uniformly high between 58°S and 63°S at about 30 uM/kg, and decreases to nearly zero at about 40°S. The concentration of silica is uniformly high at about 65 uM/kg between 59°S and 63°S, and decreases sharply between 59°S and 56°S and to nearly zero north of about 50°S. The pCO₂ data indicate that the ocean is a sink for atmospheric CO₂ north of about 50°S, whereas it is nearly neutral in the polar waters south of the Antarctic Convergence. The pCO₂ data shown in Fig. 7-B also indicate that the ocean water is undersaturated with respect to atmospheric CO₂ by as much as -60 uatm and is a CO₂ sink as far north as 17°S. These data indicate that the South Pacific subtropical gyre water between 135°W and 150.5°W is a strong sink for atmospheric CO₂ during those months investigated.

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Fig. 7 - Eight properties in the surface mixed layer along the 150.5°W meridian (WOCE P-16 section). A) Observations which were made in October- November, 1992, during the first expedition of this investigation; and B) those which were made in July-August, 1991, during the WOCE P-16C Expedition aboard the R/V Thomas Washington.



Swift (SIO), Lynne D. Talley (SIO) and Joseph Reid (SIO) who directed the three expeditions as chief scientists.

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