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**Carbon Chemistry  
of the South Atlantic Ocean  
and the Weddell Sea:**

**The Results of  
the Atlantic Long Lines (AJAX) Expeditions,  
October, 1983 - February, 1984**

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SECTION I  
EXPERIMENTAL PROCEDURES

INTRODUCTION

This report summarizes the seawater carbonate chemistry data which were obtained as part of the Long Lines (AJAX) Expedition in the South Atlantic Ocean and Weddell Sea, October-November 1983 and January-February 1984 on board the R/V KNORR. The partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) and the concentration of total dissolved carbon dioxide (total CO<sub>2</sub> or TCO<sub>2</sub>) were measured at sea on about 750 selected samples from most of the 138 hydrographic stations which were occupied during the two legs of the cruise. An additional 120 water samples were collected and analysed for TCO<sub>2</sub> in our land-based laboratory using the new technique of CO<sub>2</sub> coulometry. All the analyses were performed at least in duplicates. In addition, the total alkalinity (TALK) has been computed for all of the samples for which the necessary pCO<sub>2</sub>, TCO<sub>2</sub>, salinity and nutrient concentration values have been determined. The experimental methods used for this study, the calibration techniques and precision of the measurements are discussed in detail.

Vertical sections for the pCO<sub>2</sub>, TCO<sub>2</sub>, TALK, and apparent oxygen utilization (AOU) along the Greenwich meridian from 5° N to 70° S are presented, for the depth ranges 0-1000 meters and 0-6000 meters (Figures 7-10).

The relationships between the various measured properties are indicated on property-property plots for samples throughout the water column (Figures 11-20). The final section is a data table, presenting in tabular format the various measured and computed values mentioned above.

EXPERIMENTAL METHODS

Gas Chromatograph System for pCO<sub>2</sub> Analysis:

The equilibrator-gas chromatograph system used during the expedition for the determination of partial pressure of CO<sub>2</sub> was similar to the one which was used during the TTO-North Atlantic and TTO-Tropical Atlantic expeditions, and has been described elsewhere (Takahashi et al., 1982; Smethie et al., 1985) (see Figure 1). Briefly, water samples for analysis are drawn from the 10-liter Niskin samplers of a rosette cast directly into 500-ml narrow-necked Pyrex flasks which serve both as sample containers and equilibration vessels. The samples are poisoned with 1/4 ml of saturated mercuric chloride solution to prevent biological modification of the pCO<sub>2</sub>, and are stored in the dark until measurement, which normally was performed within 48 hours of sampling. A headspace of 3 to 5 ml was left above the water in the flasks to allow for thermal expansion during storage. The flasks are sealed air-tight using screw-caps with conical plastic liners.

Prior to analysis, the sample flasks are brought to 20.00 °C in a thermostatted water bath, and about 65 ml of the water is displaced

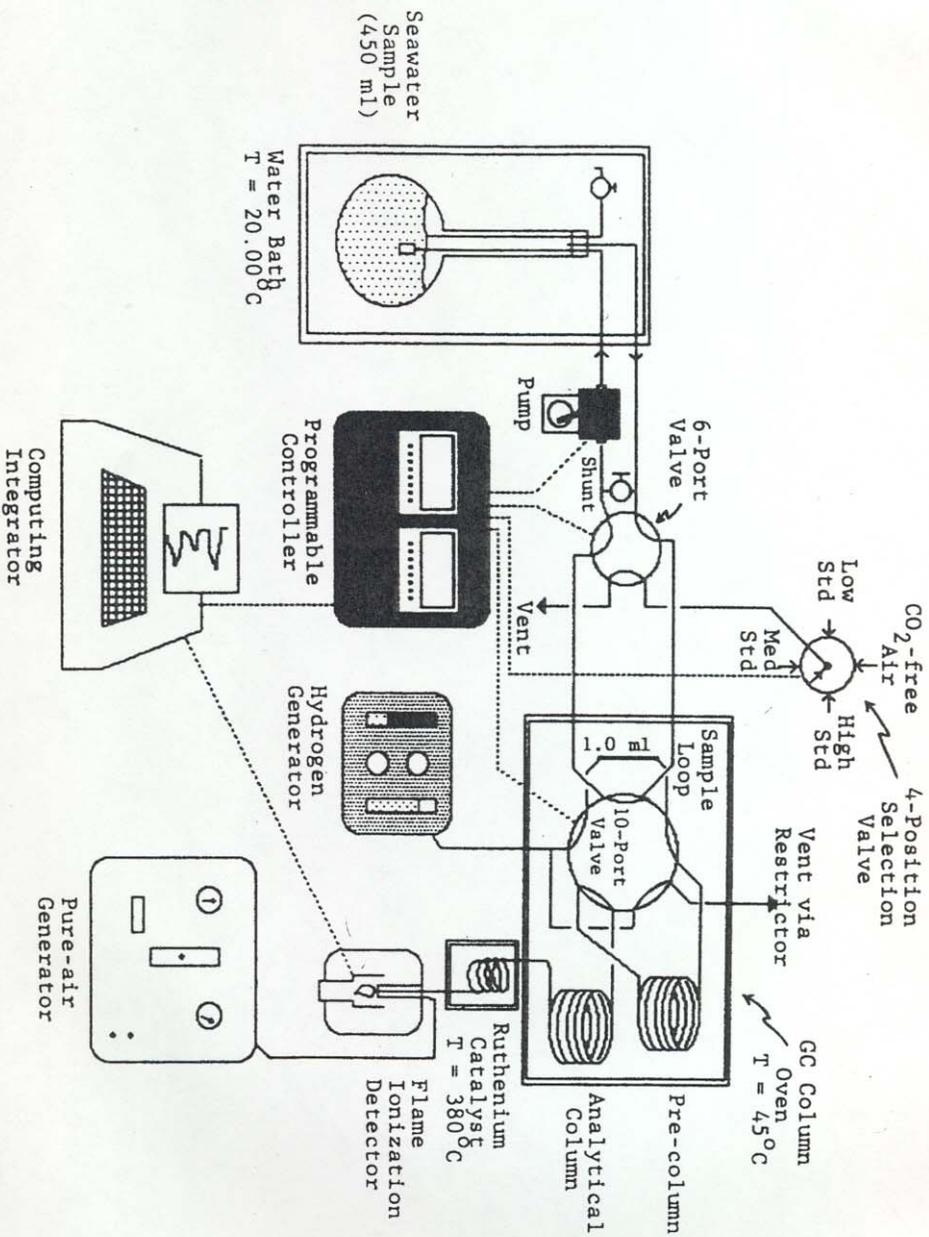


Fig. 1 Schematic diagram of gas chromatograph-based system for the determination of CO<sub>2</sub> partial pressure in seawater. Single solid lines represent gas flow pathways, dotted lines represent data and control signal paths, and solid double lines enclose thermally isolated zones. The valves are shown in the orientation they would have just after an equilibrated gas sample is injected into the carrier gas stream of the gas chromatograph for analysis. After the CO<sub>2</sub> peak elutes from the precolumn into the analytical column, the 10-port valve will be returned to its normal position, backflushing the water vapor and any hydrocarbons heavier than methane from the system while connecting the sample loop to the equilibration subsystem to prepare for the next sample.

with air of known CO<sub>2</sub> concentration. The air in the flasks and in the tubing connecting the flasks to the gas chromatograph sample loop is recirculated continuously for approximately 20 minutes, with a gas disperser about 1 cm below the water surface providing large contact area between water and air bubbles. At the end of the equilibration period, the circulation pump is switched off and the air pressure throughout the system is allowed to equalize. A 1-ml aliquot of the equilibrated air is isolated from the equilibration subsystem and injected into the carrier gas stream of the gas chromatograph by cycling the gas sampling valve to which the sample loop is attached. The gas chromatograph, a Perkin-Elmer Model Sigma-4, uses hydrogen as the carrier gas and is equipped with a 2-meter column of Chromosorb 102 to separate the CO<sub>2</sub> from the other components of the air. After separation, the CO<sub>2</sub> is converted into methane and water vapor by reaction with the hydrogen carrier in a catalytic converter of ruthenium operated at 380 °C, in a manner similar to that described by Weiss (1981), but without the use of a palladium pre-catalyst. The methane produced by this reaction is then measured with a precision of  $\pm 0.05\%$  (one standard deviation) using a flame ionization detector. The signal from the flame ionization detector is fed into a Perkin-Elmer Model Sigma-10 digital integrator, where the area of the CO<sub>2</sub> peak is computed, and the concentration of CO<sub>2</sub> in the sample is determined by comparison with the peak areas of known amounts of CO<sub>2</sub> from reference gas mixtures. The GC detector response is calibrated at least once per hour by injecting, with the same sample loop, CO<sub>2</sub>-air mixtures which are calibrated against the World Meteorological Organization standards of C. D. Keeling.

The equilibrated air samples are saturated with water-vapor at the temperature of equilibration and have the same pCO<sub>2</sub> as the water sample. By injecting the air aliquot at the pressure of equilibration and without removing the water vapor, the partial pressure of CO<sub>2</sub> is determined directly, without the need to know either the pressure of equilibration or the water vapor pressure (Takahashi et al., 1982). It is necessary to know the pressure of the calibration gas mixtures, which is done by venting the sample loop to atmospheric pressure after filling and measuring the atmospheric pressure by means of a high-accuracy electronic barometer (Setra Systems, Inc., Model 270, accuracy  $\pm 0.3$  millibars, calibration traceable to NBS provided by manufacturer). Additional corrections are required to account for the change in pCO<sub>2</sub> of the sample water due to the transfer of CO<sub>2</sub> to or from the water during the equilibration with the recirculating air, and to account for the difference in pressure between the air in the equilibrator when the pump is running and that in the GC sample loop when the pump is off. The overall precision of the pCO<sub>2</sub> measurement is estimated to be about  $\pm 0.2\%$ .

#### GC and Coulometric Systems for Total CO<sub>2</sub> Measurements:

Two independent methods were used for the measurement of total CO<sub>2</sub> (TCO<sub>2</sub>) in seawater: determination at sea using the gas chromatograph described above with a separate CO<sub>2</sub>-extraction subsystem, and that in the shore-based laboratory of stored water samples using the new technique of CO<sub>2</sub>-coulometry. Both techniques will be described below.

The gas-chromatograph system used on board the ship consisted of

an extraction system for removing the  $\text{CO}_2$  from acidified 3-ml water samples linked to the same gas chromatograph that was used for the  $\text{pCO}_2$  analyses (see Figure 2). Water samples were drawn from the Niskin samplers into 125-ml glass bottles with ground-glass stoppers, which were greased with silicone stopcock grease. The bottles were filled with three rinses and at least one volume of overflow, 2 to 3 ml of the water was removed to provide a headspace for thermal expansion, and the stoppers were held in place with strong rubber bands. About 1/8 ml of saturated mercuric chloride solution was added to prevent biological alteration of the  $\text{TCO}_2$ . An attempt was also made to draw samples using 60-ml plastic syringes equipped with plastic valves, but the samples were found to become contaminated with  $\text{CO}_2$  (presumably dissolved in the rubber end of the plunger) in a relatively short period of time, so that method was abandoned. For analysis, a metal (Hastelloy-C) sample loop of approximately 3 ml volume was filled with sample, with about 15-20 ml used for rinsing the tubing and loop, and the loop was connected to the recirculating carrier gas of the extraction system ( $\text{CO}_2$ -free air). At the same time, a 1/3 ml loop filled with 1N hydrochloric acid was similarly connected. The carrier gas forced the acid through the water-sample loop and the acidified water was then forced into a stripping column containing a coarse glass frit near the bottom. A small gas pump continually recirculated the gas through the acidified water and through a dilution volume of about 300 ml, until the  $\text{CO}_2$  was thoroughly equilibrated between water and gas and the gas was well homogenized (approximately 6 minutes). During this period, the system was connected to the sample valve of the GC, so that the sample loop was continuously flushed and contained a representative aliquot of the gas at the end of the period. Since the air recirculates through the water, a small amount (approximately 1%) of the  $\text{CO}_2$  in the system remains dissolved in the acidified water. The maximum temperature variation due to changes in room temperature, 4  $^\circ\text{C}$ , would cause a variation in the fraction of the  $\text{CO}_2$  in the water of approximately 10% of the amount retained, or about 2  $\mu\text{mol/kg}$ . The maximum salinity variation would cause a much smaller effect. Since the fraction remaining in the water is relatively small and nearly constant, the calibration procedure will allow variations in this amount of  $\text{CO}_2$  to be ignored. The circulation pump was then switched off and the gas sampling valve was switched to inject the aliquot into GC carrier gas stream. By selecting the appropriate volumes for the water sample and the dilution volume, the amount of  $\text{CO}_2$  introduced into the GC was kept close to the amount in one of the calibration gas mixtures (about 789 ppm).

In order to determine the accuracy of the shipboard  $\text{TCO}_2$  analyses, a number of samples were taken in 500-ml glass bottles with ground-glass stoppers in the same manner as the smaller samples taken for shipboard analysis. These samples were then shipped back to our shore-based laboratory for analysis using a totally independent method,  $\text{CO}_2$  coulometry. The basis of this method is described in a paper by Johnson et al. (1985). Briefly summarized, the method is as follows.

A sample of the seawater for analysis is measured by filling a calibrated sample pipet (of approximately 50 ml volume) with sufficient overflow to insure the thorough rinsing of the pipet and tubing, transferring the water to an extraction tube, acidifying, and sweeping the evolved  $\text{CO}_2$  into the cell of a  $\text{CO}_2$  coulometer with a flow



of CO<sub>2</sub>-free carrier gas. In the coulometer cell, the CO<sub>2</sub> is quantitatively absorbed by a solution of ethanolamine in dimethylsulfoxide (DMSO). Reaction of the CO<sub>2</sub> with the ethanolamine forms the weak acid hydroxyethylcarbamic acid. The pH change associated with the formation of this acid results in a color change of thymolphthalein in the solution. The color change, from deep blue to colorless, is detected by a photodiode, which continually monitors the transmissivity of the solution. The electronic circuitry of the coulometer, on detecting the change in the color of the pH indicator, causes a current to be passed through the cell, electro-generating hydroxyl (OH<sup>-</sup>) ions from a small amount of water in the solution. The OH<sup>-</sup> generated titrates the acid, returning the solution to its original pH (and hence color), at which point the circuitry interrupts the current flow. The product of current passed through the cell and time is related by the Faraday constant to the number of moles of OH<sup>-</sup> generated to titrate the acid and hence to the number of moles of CO<sub>2</sub> absorbed to form the acid.

We have calibrated the coulometer in four different ways: by injecting measured volumes of pure CO<sub>2</sub> gas at known pressure and temperature, by analysis of the CO<sub>2</sub> evolved from gravimetrically prepared solid calcium carbonate and sodium carbonate, and by injecting measured volumes of CO<sub>2</sub>-air mixtures (WMO-calibrated mixtures referred to above) at known temperature and pressure. With the exception of the last (which provides relatively small quantities of CO<sub>2</sub> and hence is susceptible to small errors in the blank determination, and which differed by 0.2%), all of the calibration techniques agreed with the electrical calibration of the instrument (i.e. independently measuring current and time and comparing with the readout) to within 0.1%. We have also observed that the calibration of the coulometer has changed by no more than 0.1% over the 2 1/2 years we have used it. With care, the coulometer is capable of a precision of better than  $\pm 1$   $\mu$ M/liter in samples of 2200  $\mu$ M/liter.

#### Atmospheric CO<sub>2</sub> measurements:

Air samples were analyzed for CO<sub>2</sub> concentration by filling the GC sample loop with air drawn from near either the ship's bow or stern (depending on the relative wind direction) using a metal-lined plastic sampling line and small bellows pump. The air sample was introduced directly into the sample loop without drying, and the excess pressure in the loop was allowed to vent to the atmosphere prior to injection into the GC for analysis. The calibration of the GC with standard gas mixtures at the same pressure allows the concentration of CO<sub>2</sub> in the sample to be computed directly. Table 1 lists the concentration of CO<sub>2</sub> in atmospheric samples taken during the two legs of the cruise. These values have been recalculated to give the concentration as a mole fraction of CO<sub>2</sub> in dried air, the mole fraction in air which is saturated with water vapor at the temperature of the sea surface, and the partial pressure of CO<sub>2</sub> in the air at the conditions of the sea surface (water saturated at sea surface temperature and at the ambient atmospheric pressure).

Table 1 Atmospheric concentration of CO<sub>2</sub> observed during the two legs of AJAX cruise. Samples were analyzed without removal of water vapor, and the concentration in dry air (VCO<sub>2</sub>) have been computed using the observed wet and dry bulb thermometer readings. The CO<sub>2</sub> concentration in air saturated with water vapor at the temperature of the sea surface (VCO<sub>2</sub>\*), and the partial pressure of CO<sub>2</sub> in water-saturated air (pCO<sub>2</sub>) at the barometric pressure which was observed at the time of analysis (pCO<sub>2</sub>) are also given.

DATE ----- (GMT) -----	TIME	LAT ----- (DEG MIN) -----	LONG ----- (DEG MIN) -----	VCO <sub>2</sub> --- (ppm) ---	VCO <sub>2</sub> *	PRESS (mb)	pCO <sub>2</sub> (uatm)
10/08/83	1800	02 59.6 N	03 46.2 W	345	333	1012.6	333
10/09/83	0945	01 30.1 N	03 37.9 W	344	334	1012.8	334
10/10/83	2200	01 30.3 S	03 20.0 W	345	335	1012.9	335
10/11/83	1630	03 00.2 S	03 12.8 W	346	336	1014.1	336
10/13/83	2200	07 33.0 S	01 07.8 W	342	333	1016.5	334
10/15/83	0100	09 45.6 S	00 46.0 E	341	333	1015.5	333
10/16/83	0300	11 59.9 S	00 51.7 E	341	333	1015.7	334
10/16/83	2000	14 00.2 S	00 57.6 E	341	334	1017.0	335
10/20/83	1830	21 01.4 S	01 19.2 E	343	335	1021.8	338
10/23/83	1230	26 59.5 S	01 39.8 E	343	335	1026.2	339
10/29/83	0930	39 00.5 S	00 59.2 E	342	337	1021.5	340
11/01/83	2100	42 48.3 S	04 52.8 E	341	337	1014.8	338
01/20/84	1900	51 50.2 S	01 11.6 E	342	339	990.0	332
01/21/84	1530	53 49.0 S	01 20.2 E	343	340	967.6	325
01/25/84	0300	61 00.2 S	00 52.7 E	343	341	993.2	334
01/25/84	2130	62 00.4 S	00 44.9 E	342	339	996.8	334
01/26/84	1500	64 00.1 S	00 20.4 E	342	340	993.9	333
01/29/84	0300	69 21.8 S	00 19.1 W	342	340	1002.6	337
02/01/84	1600	61 29.4 S	16 41.4 W	342	340	996.5	334
02/05/84	2100	58 40.9 S	26 50.6 W	341	338	1005.7	336
02/08/84	0100	56 48.5 S	34 17.8 W	341	338	983.2	328
02/13/84	0100	59 45.7 S	48 55.7 W	342	339	997.4	334
02/15/84	1300	60 48.9 S	55 38.6 W	342	340	993.9	334

## CALIBRATION AND DATA REDUCTION METHODS

The methods used to calculate  $p\text{CO}_2$  or  $\text{TCO}_2$  from raw GC peak areas differed somewhat from the procedure which was followed in the past and requires a detailed discussion. The separate parts of the procedure are: 1) calibration of the GC against two or three standard gas mixtures at known pressure, to allow the  $p\text{CO}_2$  of the air in the sample loop to be determined from the  $\text{CO}_2$  peak area; 2) for  $\text{TCO}_2$ , the relative volumes of the water sample loop, air sample loop and  $\text{CO}_2$ -extraction system are determined by measurement of the  $\text{CO}_2$  evolved from samples of gravimetrically prepared sodium carbonate solution; and 3) also for  $\text{TCO}_2$  measurements, a correction for the extraction efficiency of the stripping system was applied, using the comparison between the  $\text{TCO}_2$  measured with the GC and that measured with  $\text{CO}_2$  coulometry.

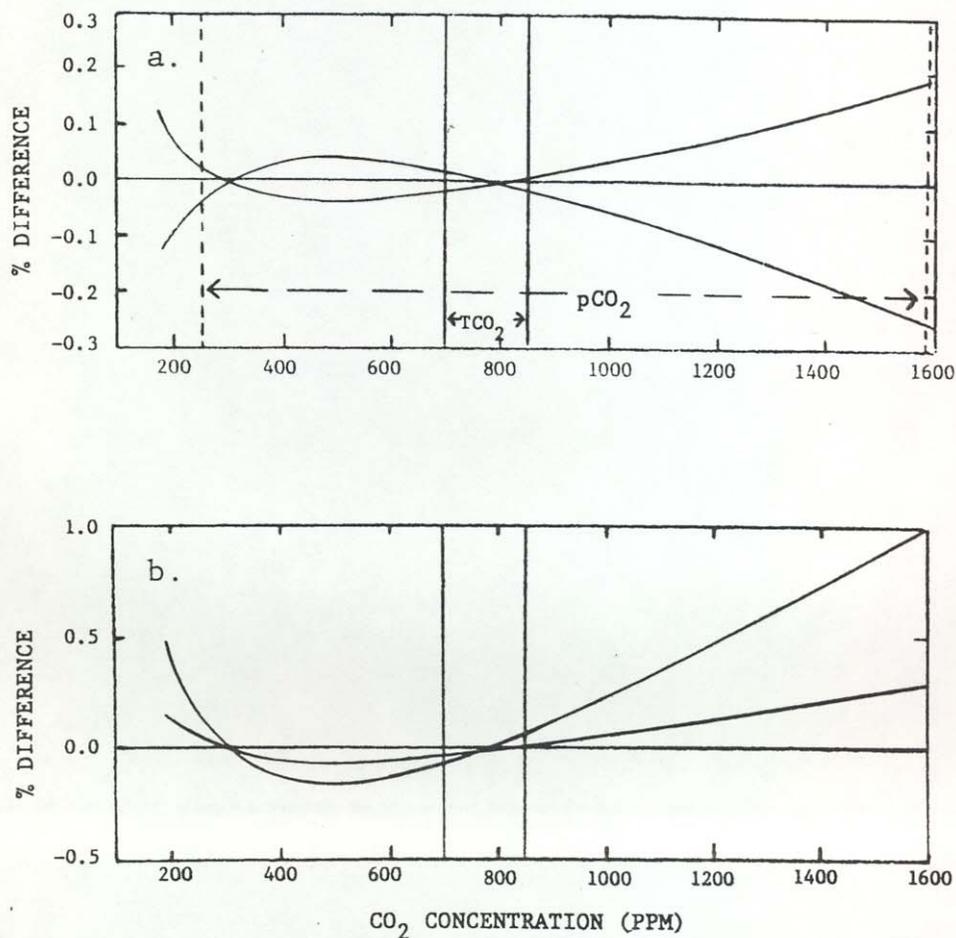
Calibration of the GC:

During Leg 1 of the expedition, the flame ionization detector (FID) response has been approximated by a straight line curve through the values of the two standard gas mixtures (294 and 789 ppm). During Leg 2, this same procedure was used for only the  $\text{TCO}_2$  analyses, while  $p\text{CO}_2$  measurements were calculated from a response curve which was parabolic and passed through the values of all three standard gas mixtures ( $\text{CO}_2$  concentrations of 294, 789 and 1388 ppm).

The response curve of a FID can be made to be very nearly linear over a wide range of concentrations. With the accumulation of deposits on the collector and with changes in the ratio of hydrogen to air feeding the flame, however, the response can become significantly non-linear. Figure 3 demonstrates the amount of error which would be introduced by the use of a linear rather than parabolic approximation to the actual detector response. The difference plotted is the concentration calculated from a parabolic curve less that calculated from a linear curve for a given peak area, divided by the "linear" concentration and multiplied by 100 to convert it into a percent difference. If the response were perfectly linear, the curve would fall on the 0.0 % difference line. As can be seen from Fig. 3-a, which applies to Leg 1 data, the maximum error resulting from using the 2-standard linear approximation is no greater than 0.25%, or 4 ppm at a value of 1600 ppm. All of the  $\text{TCO}_2$  analyses gave concentrations which were clustered closely around the concentration of the intermediate standard (789 ppm), and the maximum difference is consequently much smaller, less than 0.05% (equivalent to 1  $\mu\text{M}/\text{kg}$ ) for all samples. As shown in Fig. 3-b, the FID response curve was much more non-linear during Leg 2 compared to Leg 1 (note the change in scale of the vertical axis). During this leg, all  $p\text{CO}_2$  analyses, which range from approximately 300 to 1200 ppm, were computed using a 3-point response curve and consequently the large potential errors (up to 1% at 1600 ppm) do not apply. Only the central portion of the figure, representing the range of  $\text{TCO}_2$  analyses, is meaningful, and again the possible errors in this range are small, being no greater than 0.08% (or less than 2  $\mu\text{M}/\text{kg}$ ).

In the short term, the detector response can change rapidly in response to changes in the laboratory temperature, and occasionally this change was as great as 1% during the interval between successive calibration sequences (less than one hour). Rapid changes in the shipboard laboratory temperature were experienced as the outside door

Fig. 3 The difference between the  $\text{CO}_2$  concentrations estimated using assumed linear and parabolic detector responses. The zero reference line represents a linear fit to two calibration points, and the curved lines represent the upper and lower limits of parabolic fits to three calibration points. a.) This panel applies to the measurements during Leg I. The vertical dashed and solid lines indicate the ranges of measured  $\text{pCO}_2$  and  $\text{TCO}_2$  values respectively. It is seen that the difference between the two-point linear calibration and the three-point parabolic calibration is small: less than 0.02% for  $\text{TCO}_2$  and less than 0.2% for  $\text{pCO}_2$ . b.) The curves represent the upper and lower limits observed during Leg II, indicating that the detector response during Leg II was more non-linear than that during Leg I. Therefore, for the  $\text{pCO}_2$  measurements during Leg II, parabolic fits to three calibration points were used. For the  $\text{TCO}_2$  measurements demarked by solid vertical lines, linear fits to two calibration points were used.



was often opened to reduce the level of freon contamination in the laboratory air. In order to reduce the effects of this change in detector response, we assume that the detector drift is linear with time and compute the detector response curve (either linear or parabolic) using the drift-corrected peak areas for the standard gas mixtures at the time of injection of the unknown by interpolating between the analyses of each standard from the calibration sequences preceding and following the unknown.

#### Calibration of TCO<sub>2</sub> extraction system:

The number of moles of CO<sub>2</sub> in the GC sample loop at the time of injection of a TCO<sub>2</sub> sample is a function of the volume of the GC sample loop, the volume of seawater metered into the extraction system by the seawater sample loop, and the temperature and volume of the gas volume of the extraction system, as well as the concentration of CO<sub>2</sub> in the seawater sample. The temperature of the GC sample loop is constant, being located in the well-thermostatted GC column oven, and the remainder of the gas volume of the extraction system is submerged in a water bath, the temperature of which is monitored and recorded at the time of injection of each sample. Rather than determine the absolute volumes of the various parts of the extraction system, we have chosen to use solutions of known CO<sub>2</sub> concentration to establish the relationship between CO<sub>2</sub> concentration of the sample and the number of moles of CO<sub>2</sub> in the sample loop at the time of injection into the GC. Sodium carbonate powders (dried at 180 °C in air for about 16 hours) were weighed in our land-based laboratory, wrapped in aluminum foil, sealed in air-tight plastic vials and stored in silica gel desiccant for use in checking the extraction system during the cruise. At sea, solutions of known CO<sub>2</sub> concentration were prepared by opening the foil packets and placing the entire packet in a volumetric flask filled to the reference line with low-CO<sub>2</sub> water. During Leg 1, this water was prepared by stripping distilled water with CO<sub>2</sub>-free air overnight; during Leg 2 it was found to be much easier to prepare the water as needed by passing water from the ship's evaporator through a pair of deionization columns (Cole-Parmer Research cartridge or equivalent). Regardless of the method used to produce the water, the concentration of CO<sub>2</sub> was checked by running an aliquot as an unknown, and the final concentration of CO<sub>2</sub> in the standard solutions was corrected for this residual CO<sub>2</sub>. The standard solutions, once made up, could not be successfully stored for more than a few hours, and consequently only the initial calibration determined from a given solution was used. During the second leg of the expedition, drift in the calibration of the extraction system, possibly due to a progressive fouling of the seawater sample loop, amounted to a nearly linear decrease of about 0.75% over a period of 33 days. Due to difficulty experienced in preparing standard solutions on shipboard during the first leg, the drift during that leg is not as certain, but appears to have been of a similar magnitude as during the second leg. All TCO<sub>2</sub> values have been corrected for this apparent change in the calibration factor of the extraction system by fitting the calibration factors computed from all calibration runs with a linear regression against cumulative run number, then using the equation of the resulting line to calculate system calibration factor to be applied to each analysis. Since all the calibration runs have been used to

establish the calibration curve, only the effects of long-term variation in the volumes of the extraction system are removed by this procedure, while those due to short-term variations, such as in the extraction efficiency, may remain.

#### Extraction efficiency correction:

A more serious problem than the long-term drift of the calibration factor of the extraction system was an occasional slight decrease in the extraction efficiency, apparently due to the accumulation of salt on the check valves of the circulation pump. Whenever the pumping rate was sufficiently reduced to be obvious, the pump was disassembled and cleaned, but before this stage was reached, the extraction efficiency appears to have been reduced to such an extent that the amount of time allowed for the extraction was insufficient, and the amount of CO<sub>2</sub> in the recirculating gas was slightly low. This effect was not noticed during the cruise, but became evident when the TCO<sub>2</sub> measurements made by GC were compared with the coulometric analyses made on stored duplicate samples. There are three arguments which support the superiority of the coulometer data. First, as mentioned earlier, our coulometer calibration is consistent with four independent methods and does not appear to change with time. Secondly, the coulometer data are more precise (i.e.  $\pm 0.9$   $\mu\text{M}/\text{kg}$ , as shown in Figure 5). Thirdly, our long-term sample storage tests show that the total CO<sub>2</sub> concentration in the poisoned samples is stably preserved for several months. For these reasons, we believe that the coulometric analyses of stored samples from the cruise give accurate values, and where these values do not agree with the shipboard GC values we feel justified in correcting the latter. We have attempted to correct the GC analyses for this effect by calculating the average difference between GC and coulometric analyses for blocks of GC analyses (all the analyses made during one analytical session, between periods when the GC was being used for pCO<sub>2</sub> analysis) and applying to the GC values as a multiplier the factor necessary to make this average difference equal zero. The largest correction required was less than 1.5%, and in general the correction was less than 0.3%.

Figure 4 shows a comparison of the coulometer TCO<sub>2</sub> data with the GC TCO<sub>2</sub> values thus corrected. A 1:1 linear correlation is observed. The r.m.s. deviation of the data points about this trend line is approximately  $\pm 5.4$   $\mu\text{M}/\text{kg}$ . This represents a realistic estimate of the over-all precision including the inter-station variability. However, as shown in Figure 5, the intra-station precision of the GC analyses is about  $\pm 3$   $\mu\text{M}/\text{kg}$  (root mean square deviation).

#### COMPARISON WITH THE RESULTS OF OTHER EXPEDITIONS

Figure 5 shows a plot of TCO<sub>2</sub> versus depth for a location at approximately 60° S, 1° E observed during the following three expeditions: Station 83 and 84 of this cruise (AJAX, 24 January 1984), GEOSECS Station 89 (23 January 1973) and Station 241 of the 1986 Winter Weddell Sea Project (WWSP, 18 July 1986). The GEOSECS TCO<sub>2</sub> values, as determined using the potentiometric alkalinity titrator, have been plotted as originally reported. However, a recent comparison

Fig. 4 Comparison of the values of total CO<sub>2</sub> concentration (TCO<sub>2</sub>) determined on duplicate pairs of samples by means of gas chromatography (GC) and shore-based coulometry. The coulometric measurements have been used to provide the over-all calibration of the GC-based system; consequently the points necessarily plot near the 1:1 line. Most of the scatter of the data points about this line (i.e. a r.m.s. deviation of 5.4  $\mu\text{M}/\text{kg}$ ) is attributed to random errors in the GC-based measurements.

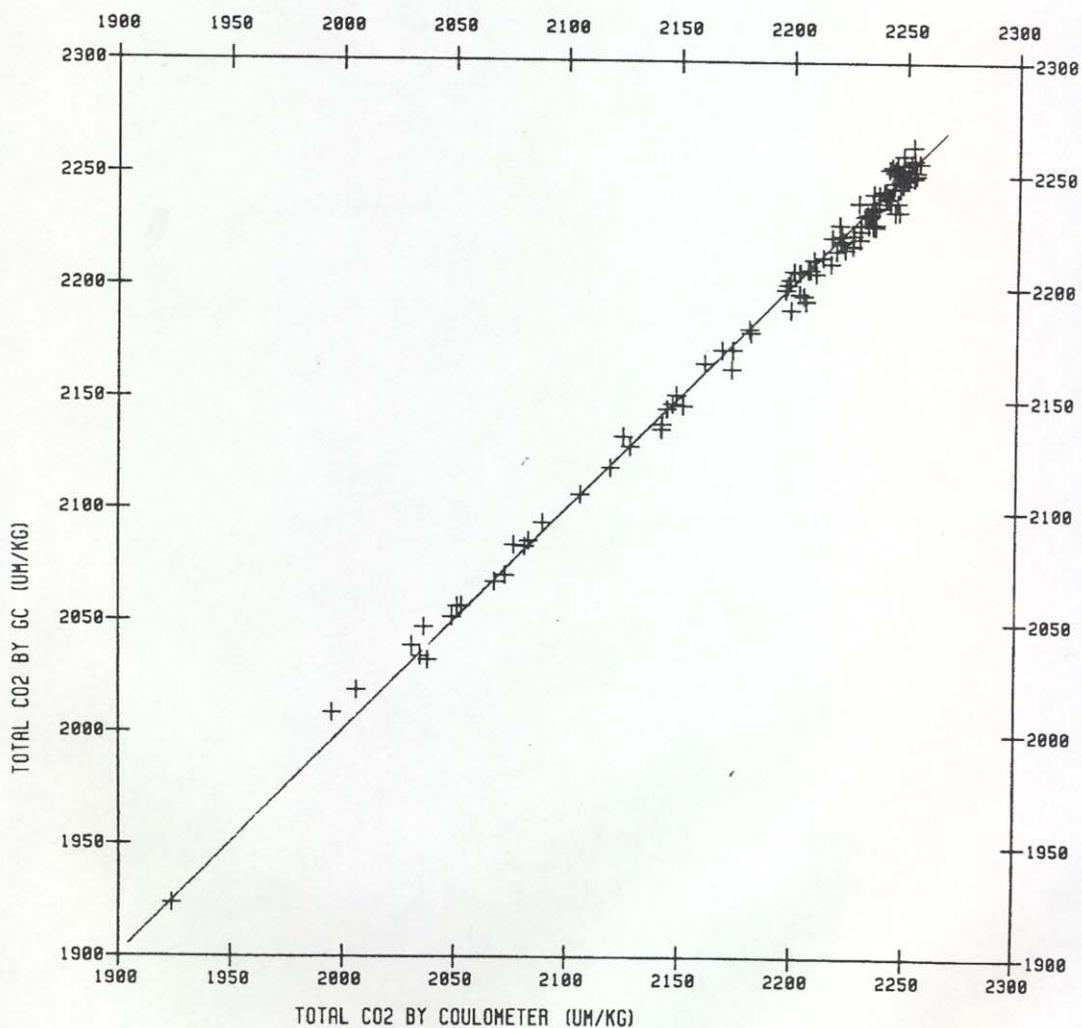
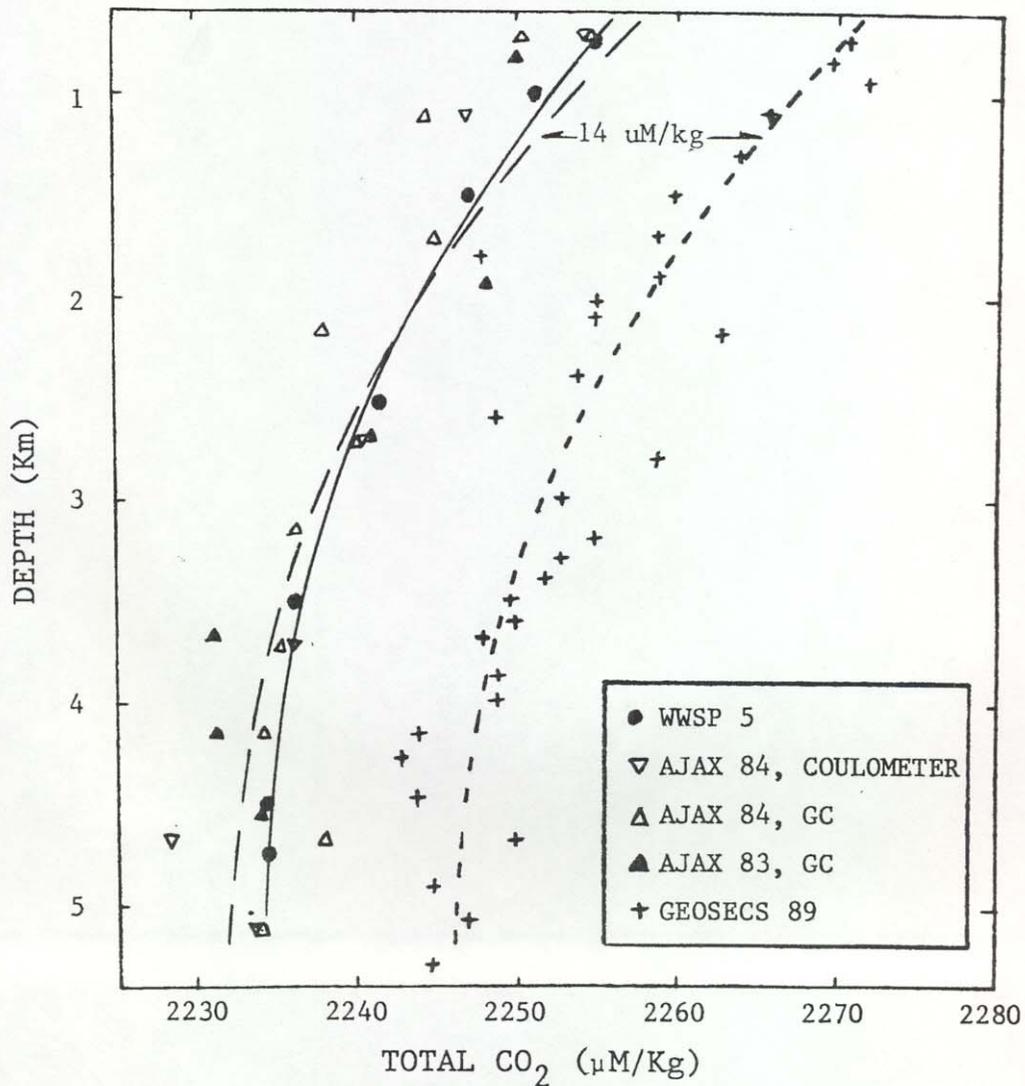


Fig. 5 Comparison of the total  $\text{CO}_2$  concentration data obtained at GEOSECS Station 89, Winter Weddell Sea Project (WWSP) Station 5 and Long Lines (AJAX) Station 83 and 84. These stations are located at about  $60^\circ\text{S}$  and  $1^\circ\text{E}$ . The GEOSECS data (+) were obtained by means of a potentiometric titration method; the WWSP data (●) were obtained by means of a coulometric method; and the AJAX data were obtained by means of GC ( $\Delta$  and  $\blacktriangle$ ) and coulometric ( $\nabla$ ) methods. The solid curve indicates a parabolic least squares fit to the seven WWSP data points with a r.m.s. deviation of about  $0.9 \mu\text{M/kg}$ . The AJAX data, although scatter more widely, are consistent with the WWSP data. The short-dashed curve represents a parabolic least squares fit to the GEOSECS data with a r.m.s. deviation of about  $4 \mu\text{M/kg}$ . When the GEOSECS data are corrected by  $-14 \mu\text{M/kg}$  as suggested by Takahashi et al. (1986), the corrected values are consistent with the WWSP data as indicated by the long-dashed curve.



of the GEOSECS  $\text{TCO}_2$  measurements in the North Atlantic with those computed from the alkalinity and  $\text{pCO}_2$  measurements made at the same location during the TTO/North Atlantic Study indicates that the Atlantic GEOSECS  $\text{TCO}_2$  values are systematically in error and need to be corrected by subtracting a constant 14 micromoles/kg (Takahashi et al., 1985). Dashed curves on the figure represent the least squares parabolic fit to the GEOSECS  $\text{TCO}_2$  data points for all depths greater than 750 meters (short dashes for the original analyses, long dashes for the points corrected by  $-14 \text{ uM/kg}$ ). The WWSP  $\text{TCO}_2$  values were obtained recently using shipboard  $\text{CO}_2$  coulometry (Chipman and Takahashi, 1986, unpublished data) and are completely independent of the GEOSECS and TTO/NAS data sets. For comparison, the seven WWSP data points from a similar depth range have likewise been fitted with a least squares parabola, shown on the figure as a solid curve. The superior quality of this data set is demonstrated by the r.m.s. deviation of  $\pm 0.9 \text{ uM/kg}$  for this parabolic fit. The near coincidence of these two concentration profiles (average difference between the curves at depths greater than 700 meters is  $-0.4 \pm 3.7 \text{ uM/kg}$ ) gives confidence that the correction applied to the GEOSECS data is indeed justified. The stored  $\text{TCO}_2$  samples from AJAX Station 84, analyzed by coulometry, plot at slightly lower concentrations than the WWSP samples, with an average offset of about  $-1.7 \pm 2.8 \text{ uM/kg}$  for the six samples. The shipboard GC analyses from this station show very close agreement with the other analyses, with the average deviation from the WWSP trend being  $-1.7 \pm 3.0 \text{ uM/kg}$ . In addition, the analyses from Station 83, which is located within one degree of Station 84, similarly agree very well (average difference is  $-1.0 \pm 3.4 \text{ uM/kg}$ ). Although the GC values for both of these stations have been plotted as corrected using the coulometric analyses, the correction increased the values by less than  $1 \text{ uM/kg}$ , and consequently the agreement with the other data sets is meaningful.

## REFERENCES TO SECTION I

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## SECTION II

## MERIDIONAL PROFILES OF CARBON CHEMISTRY

## AND APPARENT OXYGEN UTILIZATION

ALONG THE PRIME MERIDIAN,  $4^{\circ}\text{N} - 70^{\circ}\text{S}$ 

- Fig. 6 Station locations for the Long Lines (AJAX) Expedition, October, 1983 through February, 1984.
- Fig.7-a Meridional distribution of the total  $\text{CO}_2$  concentration ( $\mu\text{M}/\text{kg}$ ) along the prime meridian, 0-1000 meters
- Fig.7-b Meridional distribution of the total  $\text{CO}_2$  concentration ( $\mu\text{M}/\text{kg}$ ) along the prime meridian, 0-6000 meters
- Fig.8-a Meridional distribution of  $\text{pCO}_2$  ( $\mu\text{atm}$ ) in seawater at  $20^{\circ}\text{C}$  along the prime meridian, 0-1000 meters
- Fig.8-b Meridional distribution of  $\text{pCO}_2$  ( $\mu\text{atm}$ ) in seawater at  $20^{\circ}\text{C}$  along the prime meridian, 0-6000 meters
- Fig.9-a Meridional distribution of the total alkalinity ( $\mu\text{eq}/\text{kg}$ ) along the prime meridian, 0-1000 meters
- Fig.9-b Meridional distribution of the total alkalinity ( $\mu\text{eq}/\text{kg}$ ) along the prime meridian, 0-6000 meters
- Fig.10-a Meridional distribution of the apparent oxygen utilization ( $\mu\text{M}/\text{kg}$ ) along the prime meridian, 0-1000 meters
- Fig.10-b Meridional distribution of the apparent oxygen utilization ( $\mu\text{M}/\text{kg}$ ) along the prime meridian, 0-6000 meters

Fig. 6 Station locations for the Long Lines (AJAX) Expedition.

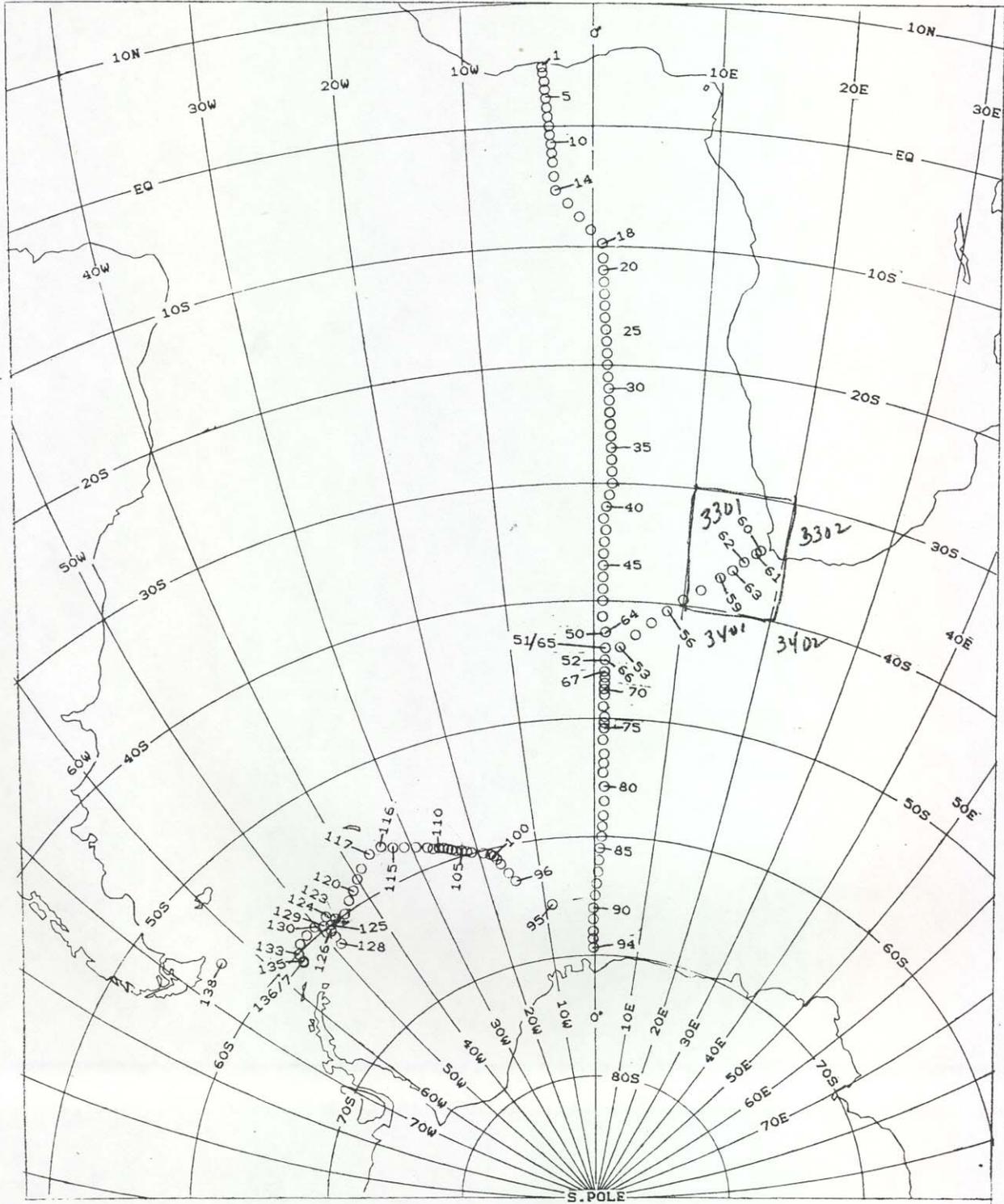


Fig. 7-a Meridional distribution of the total CO<sub>2</sub> concentration (uM/kg) in seawater along the prime meridian, 0 - 1000 meters.

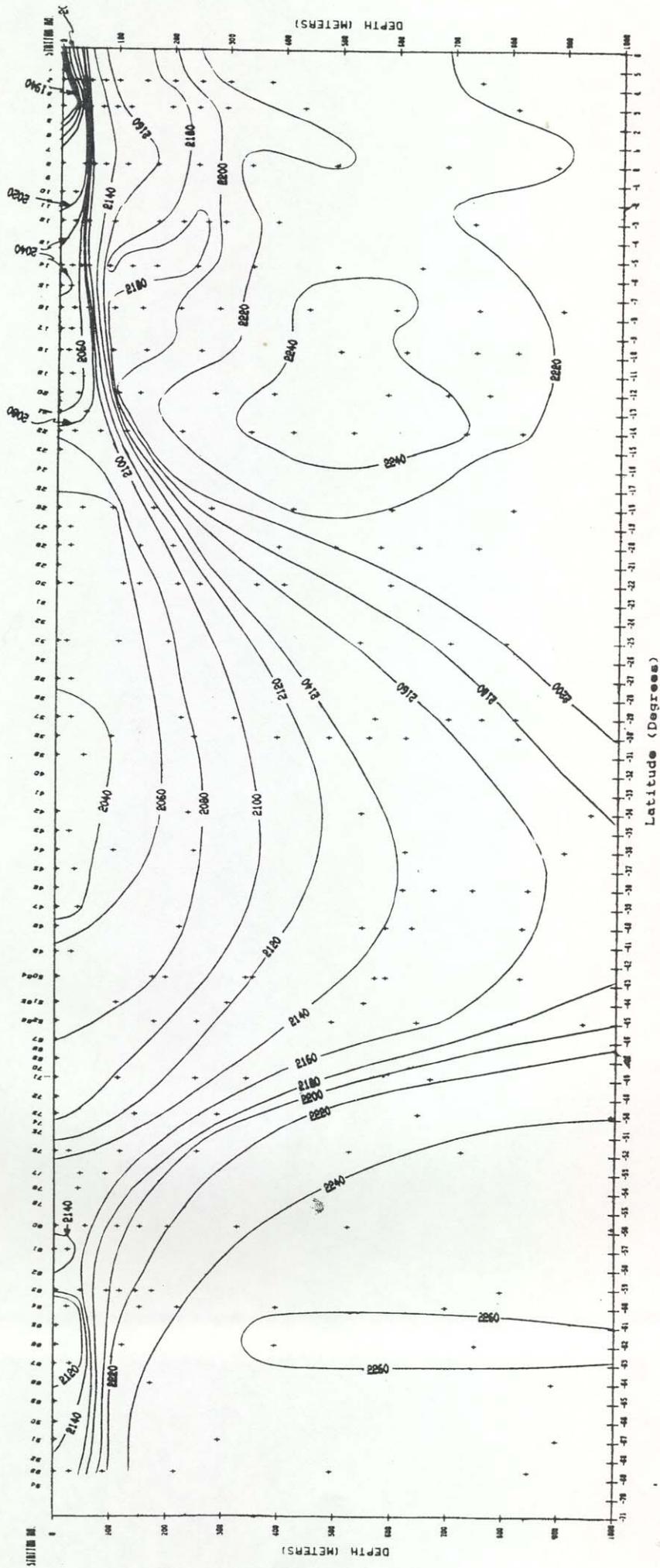
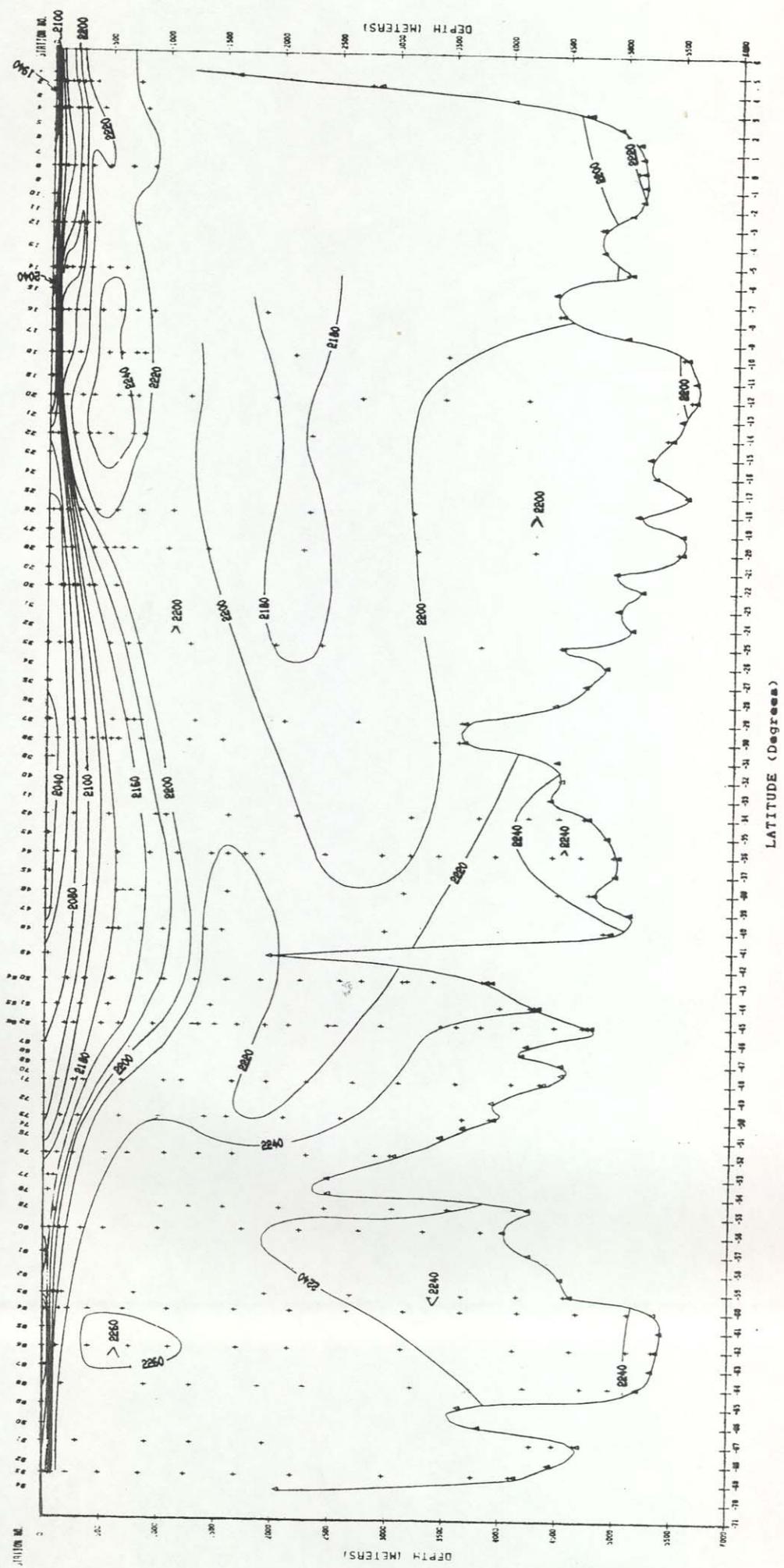


Fig. 7-b Meridional distribution of the total CO<sub>2</sub> concentration (uM/kg) in seawater along the prime meridian, 0 - 6000 meters.



DEPTH (METERS)

LATITUDE (Degrees)

Fig. 8-a Meridional distribution along the prime meridian of  $pCO_2$  (uatm) in seawater at  $20^\circ C$ , 0 - 1000 meters.

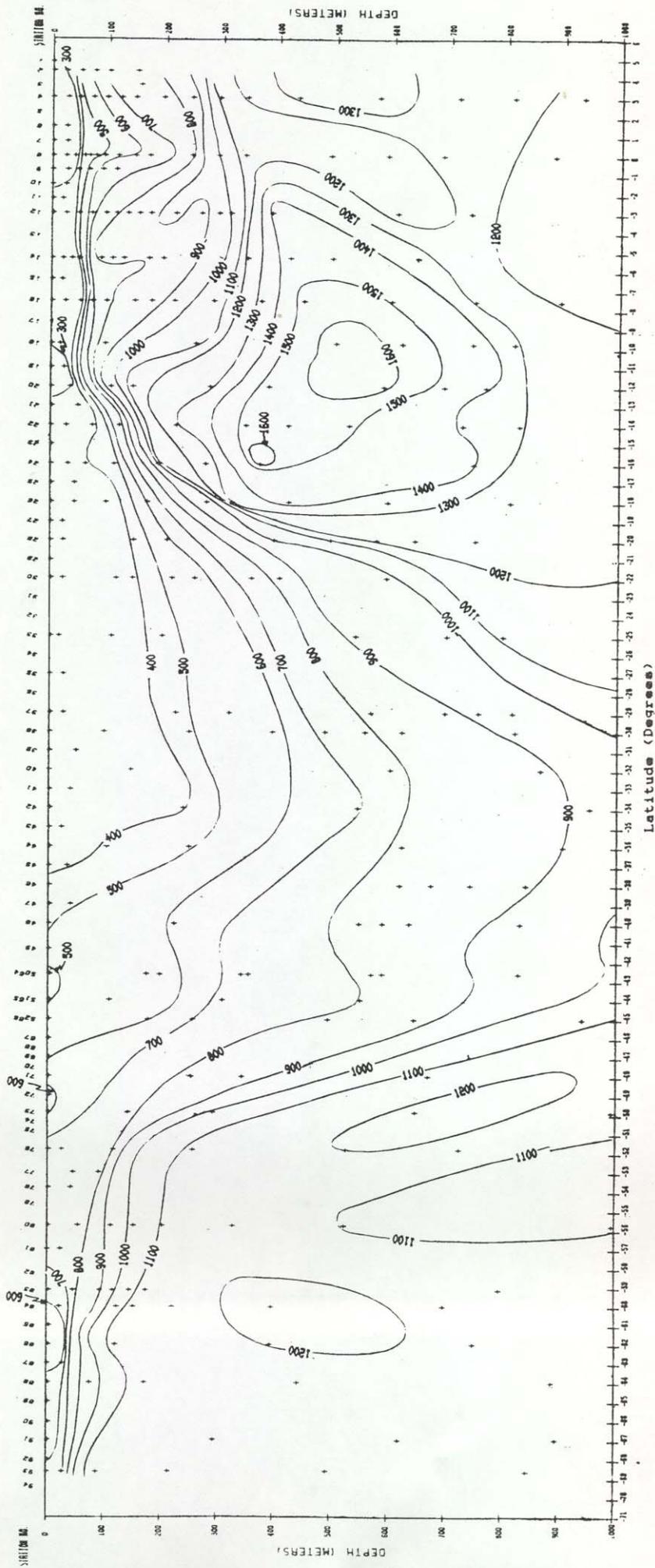


Fig. 8-b Meridional distribution along the prime meridian of  $pCO_2$  (uatm) in seawater at  $20^\circ C$ ,  
 0 - 6000 meters.

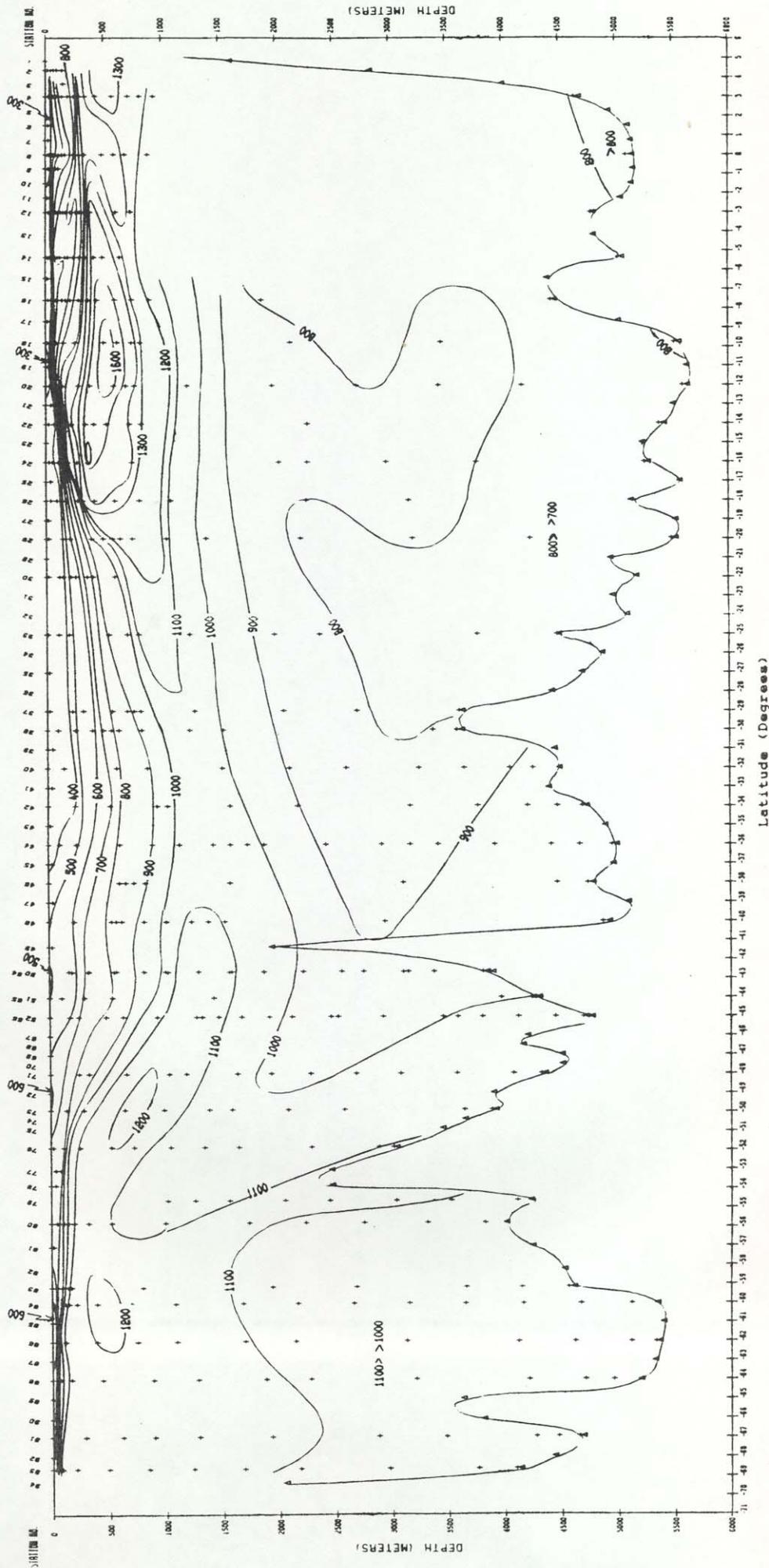


Fig. 9-a Meridional distribution along the prime meridian of the total alkalinity (ueq/kg) in seawater, 0 - 1000 meters.

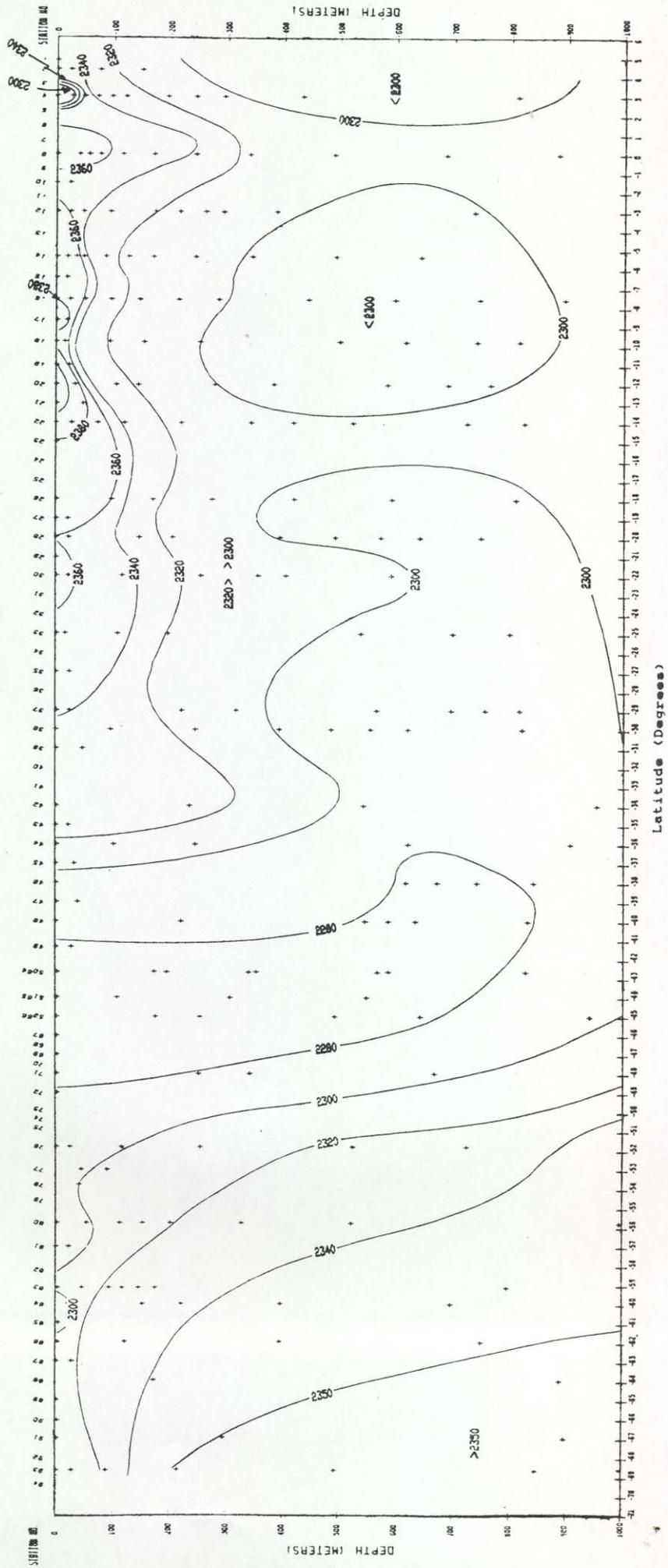


Fig. 9-b Meridional distribution along the prime meridian of the total alkalinity (ueq/kg) in seawater, 0 - 6000 meters.

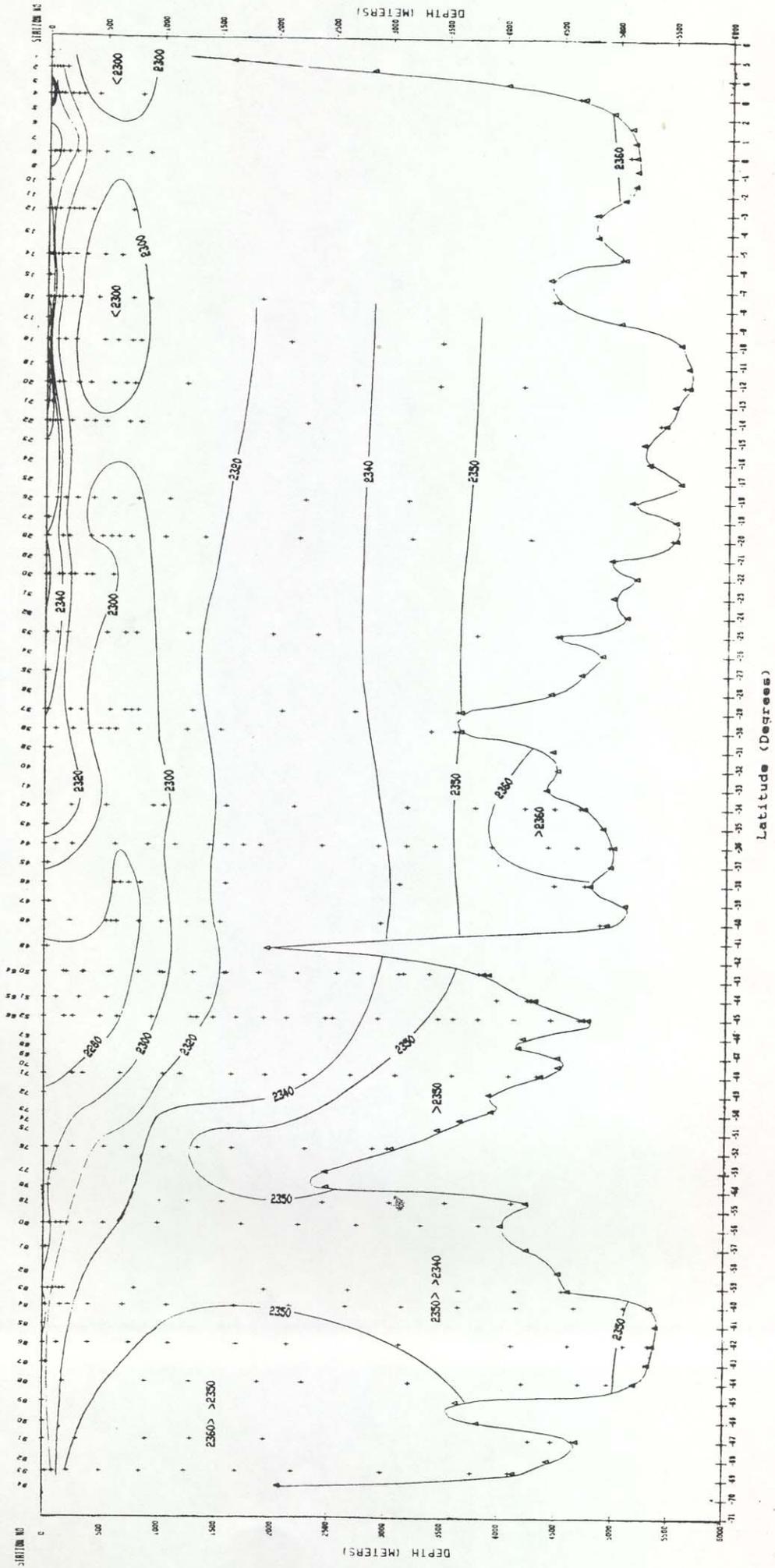


Fig. 10-a Meridional distribution along the prime meridian of the apparent oxygen utilization, AOU, in seawater ( $\mu\text{M}/\text{kg}$ ), 0 - 1000 meters.

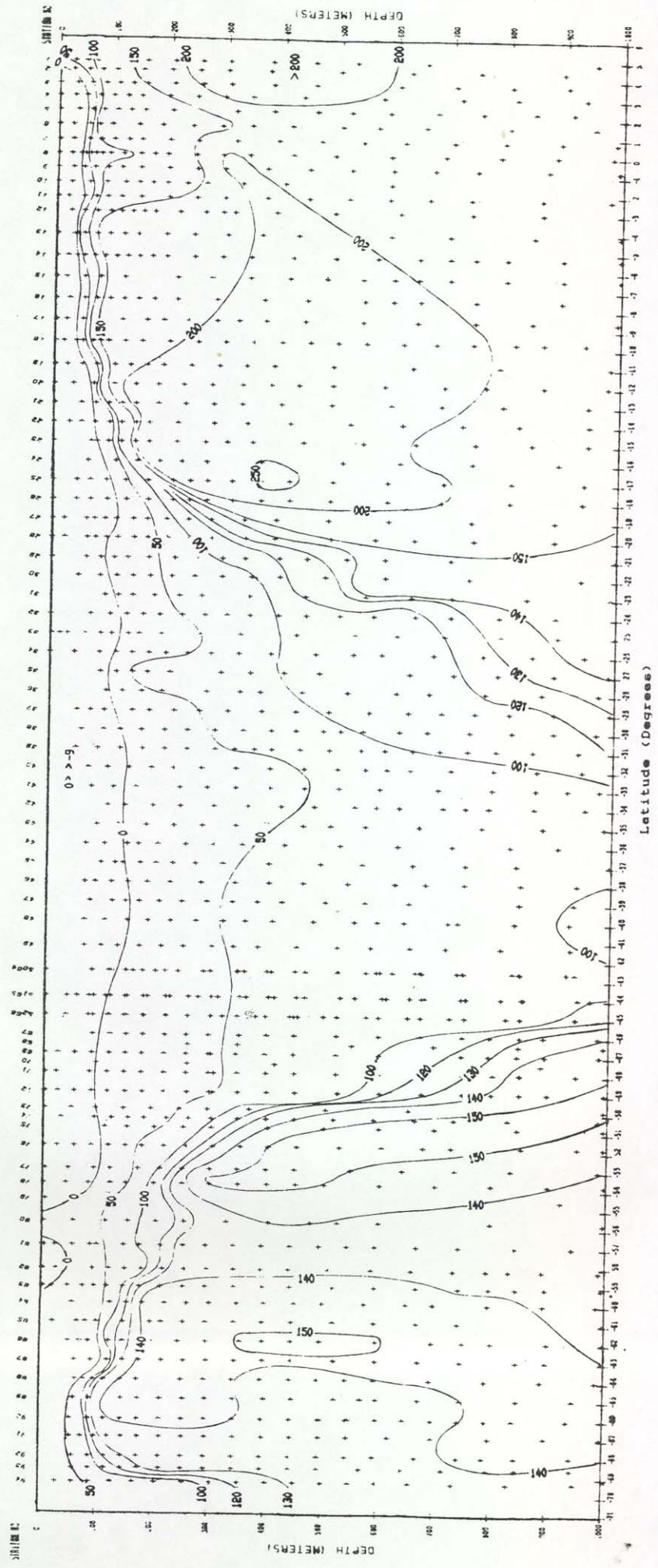


Fig. 10-b Meridional distribution along the prime meridian of the apparent oxygen utilization, AOU, in seawater ( $\mu\text{M}/\text{kg}$ ), 0 - 6000 meters.

