CRUISE REPORT: AJAX

(Updated JAN 2011)
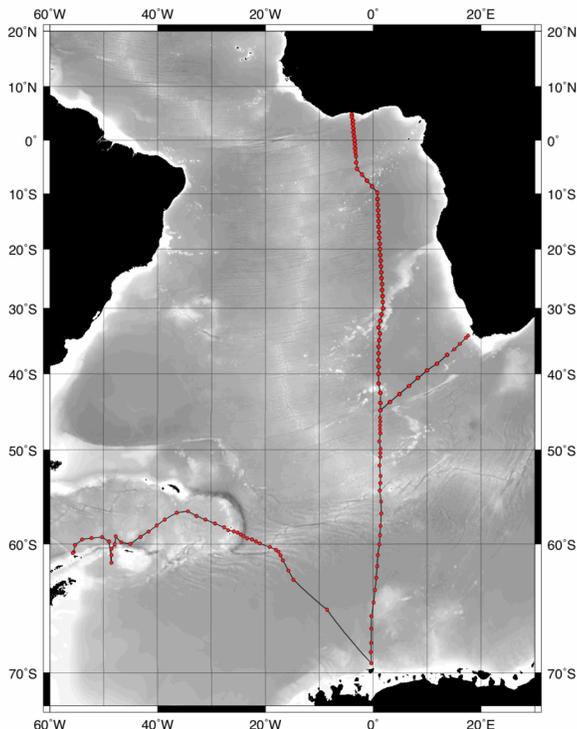
HIGHLIGHTS

Cruise Summary Information

Section designation	AJAX leg 1	AJAX leg 2
ExpoCodes	**316N19831007**	**316N19840111**
Chief Scientists	**Joseph L. Reid/SIO** Scripps Institution of Oceanography 9500 Gilman Drive, MS 0230 La Jolla, CA 92093-0230 Tel: 858-534-2055 Email: jreid@ucsd.edu	**Worth D. Nowlin, Jr./TAMU** Texas A&M University O&M Building, Room 713 MS 3146 College Station, Texas 77843 Tel: 979.845.3900 Fax: 979.847.8879 Email: wnowlin@tamu.edu
Dates	7 OCT - 6 NOV 1983	11 JAN - 19 FEB 1984
Ship	R/V *KNORR*	R/V *KNORR*
Ports of call	Abidjan, Ivory Coast to Cape Town, South Africa	Cape Town, South Africa to Punta Arenas, Chile
Geographic boundaries	4° 49' 40.8" N 3° 57' 46.8" W 1° 49' 58.8" E 41° 21' 10.8" S	44° 0' 57.6" S 0° 25' 12" W 1° 28' 12" E 69° 21' 46.8" S
Stations	49	31
Floats and drifters	0	0
Moorings	0	0

LINKS TO TEXT LOCATIONS

Shaded sections are not relevant to this cruise or were not available when this report was compiled

AJAX • 1983-84 • Reid/Nowlin • R/V *Knorr*

PHYSICAL, CHEMICAL AND IN-SITU CTD DATA

INTRODUCTION
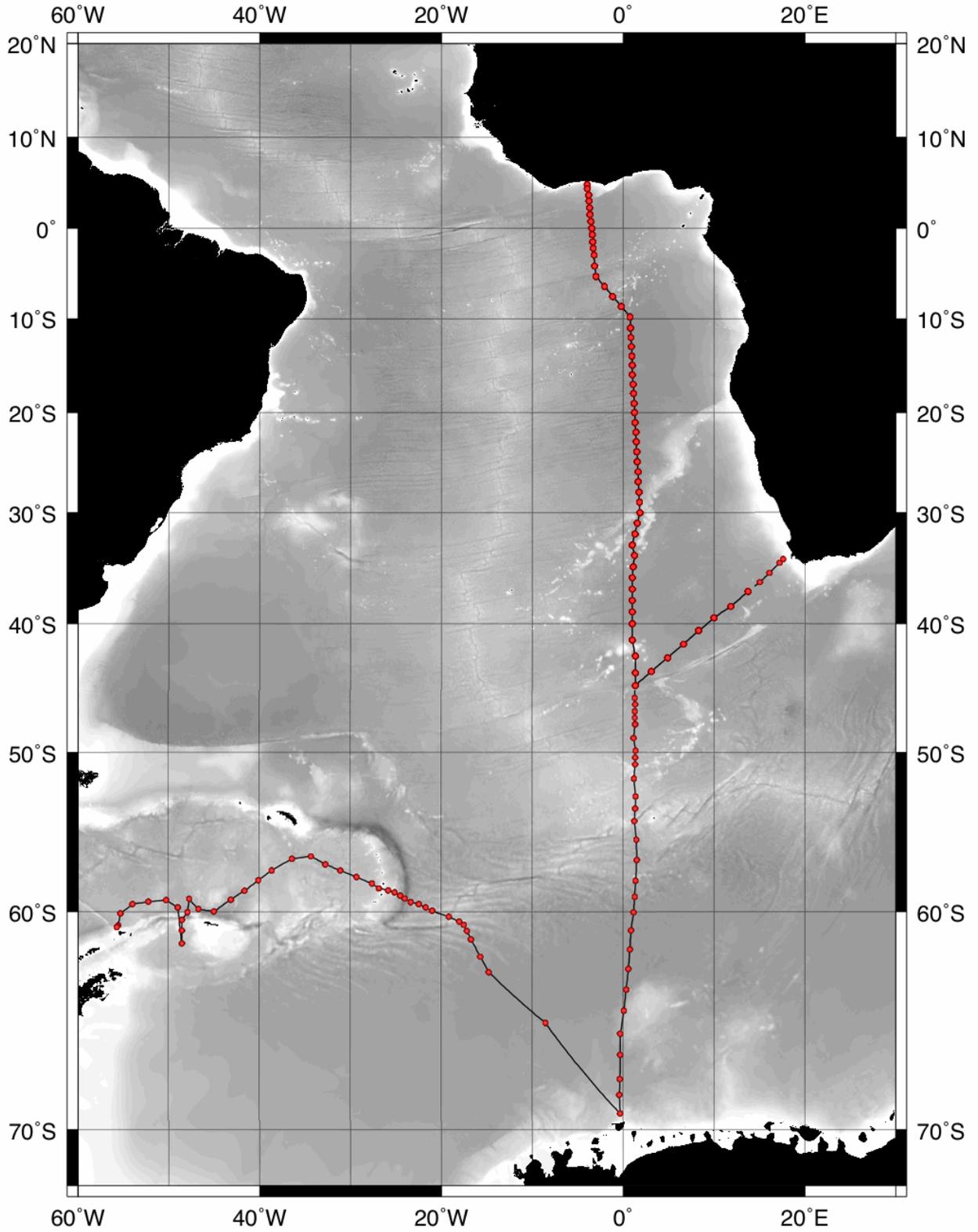
This data report presents hydrographic and CTD data collected aboard the R/V *Knorr* on Ajax Expedition Leg I, Abidjan, Ivory Coast to Cape Town, South Africa (7 October - 6 November, 1983), and on Leg II, Cape Town to Punta Arenas, Chile (11 January -19 February, 1984). Ajax Expedition was jointly funded by the National Science Foundation and the Office of Naval Research. The expedition objectives were to provide data on the general circulation of the South Atlantic, Weddell Gyre and the Scotia Sea. A line of hydrographic stations, with sampling from the surface to the bottom on most stations, was occupied along the Greenwich meridian from the coast of Africa at 5°N to the Antarctic ice edge at 69°S, and from there across the Scotia Ridge and through the Scotia Sea (Figure 1). In addition to the hydrographic measurements of temperature, salinity, oxygen and nutrients given in this report, water samples were also collected for analyses of other tracers such as Freons 11 and 12, tritium and helium-3. Table 1 summarizes the various ancillary measurements and lists the principal investigators.

The hydrographic data were, for the most part, collected and processed at sea by personnel of the Physical and Chemical Oceanographic Data Facility (PACODF) of Scripps Institution of Oceanography. Final adjustments to the hydrographic data and CTD processing were completed after the cruise. Tapes of the hydrographic data and CTD data at one-decibar intervals have been sent to the National Oceanographic Data Center.

STANDARD PROCEDURES

IN-SITU CONDUCTIVITY/TEMPERATURE/DEPTH (CTD) - ROSETTE CAST DATA

Most stations consisted of two CTD-rosette casts to collect water samples from 36 or more levels from the sea surface to near the bottom. A rosette frame holding 24 10-liter PVC plastic bottles was lowered with the CTD probe, and the bottles were closed during the up cast at depths selected on the basis of temperature, salinity and oxygen features observed on the down cast CTD plots. The deep cast usually tripped 23 bottles from near the bottom up to less than 1000 meters. The 24th bottle was tripped at the surface to provide calibration checks for the CTD. The shallow cast typically overlapped one level of the deep cast and sampled an additional 12 levels up to the surface. Occasionally, more than one bottle was tripped at one level to provide additional water for other tracer analyses. Also, on some stations water was taken from the surface CTD check bottle of the deep cast for special chemical analyses. As the hydrographic data from these duplicate levels do not provide additional useful information on the water

column characteristics, they have been omitted from this data report. Similarly, data from a few wire casts with special samplers for trace elements are not included.

Pressure and temperature for the discrete levels are from the corrected CTD data taken at the time of the rosette bottle trip. The CTD pressure and temperature offsets were monitored by comparisons with deep-sea-reversing thermometers (DSRTs) mounted in at least three reversing racks per rosette cast. Two different CTDs were used on the expedition. The pressure sensor on one of the CTDs used on the first leg had a serious hysteresis problem between the down and up casts with surface offsets of 10 to 20 db different at the end of the cast compared to the beginning of the cast. The problem has been isolated to just the near-surface levels on the up cast and the data have been corrected. The pressure sensor was replaced at the beginning of the second leg. The new sensor had a much larger slope adjustment as function of pressure, but it behaved in a consistent manner. Corrections to the CTD pressures were based upon laboratory pressure calibrations and upon the CTD pressure offset observed as the CTD entered the water. Comparisons with the pressure obtained from unprotected DSRTs, though monitored, were not used because the CTD pressure sensor and the lab pressure calibration apparatus are considered to be more sensitive than unprotected mercury thermometers.

Depth was calculated from pressure by Saunders' method (1981). Pressure is also given for reference.

The CTD temperature corrections were based primarily upon comparisons with special deep low-range DSRTs. A two-point (0°C and at ambient temperature above 20°C) laboratory temperature calibration was performed on both CTDs prior to the cruise. However, the laboratory calibration was not very useful for two reasons: the ambient check differed by several milli-degrees on successive days, when the bath temperature differed by about one degree, and a two-point calibration is not adequate to determine the CTD temperature non-linearity over the full temperature range of the instrument. The DSRT checks on CTD temperature sensor were not entirely satisfactory either. Because of the differing time responses of the two methods for measuring temperature and the depth separation between the CTD temperature probe and the DSRT rack mounted on the plastic bottles above the probe, the DSRTs do not provide very useful calibration data at shallower depths where the local temperature gradient exceeds .01°C per meter. The most useful in-situ CTD checks are in isothermal layers such as in the surface mixed layer, or in the low temperature gradients in the deep water. The surface DSRTs were often higher-range, lower-precision thermometers which are read to the nearest 0.01°C. The deeper DSRT racks contained low-range thermometers which were read to the nearest 0.001°C and they provided the data for the primary CTD temperature offset corrections. The temperature data in this report are listed to the nearest 0.001°C, but the uncertainty is several milli-degrees, especially in the warmer regions of the water column.

Salinity samples were collected from each rosette bottle and analyzed usually within two days on an Autosal inductive salinometer. Wormley Standard Seawater (SSW) batch P92 was used to standardize the salinometer on stations 60 through 116, batch P90 was used on the remaining stations. After the cruise, a problem was discovered on another salinometer: the machine had a jump in conductivity ratio when the suppression dial was changed from the 1.9 (S < 35) to 2.0 (S > 35) setting. Closer examination of the Ajax salinity data revealed that one of the two salinometers used at sea definitely had a similar problem. The deep and bottom water salinities less than 35 listed in this report are correct relative to the SSW, but salinities greater than 35 may have a systematic offset of .002 to .003 salinity.

Comparison of the bottle salinities with CTD salinities was used to identify malfunctioning rosette bottles and to verify that water samples used for other chemical analyses were collected from the correct depth without contamination by leakage of the rosette bottle or from a mis-trip. The rosette sample bottles malfunctioned often, most frequently due to lanyards caught in the lids. In such cases, all water sample analyses were deleted and the erroneous salinity replaced with a corrected CTD value followed by the

footnote letter "D". All salinity values were calculated from the algorithms for the Practical Salinity Scale, 1978 (UNESCO, 1981) and are listed to three decimal places.

Dissolved oxygen was determined by the Winkler method as modified by Carpenter (1965), using the equipment and procedure outlined by Anderson (1971). In the hands of a skilled operator, this technique is capable of a precision of better than 0.01 ml/l O_2. In practice, the error may be several times larger than that figure. In the early part of the first leg, the micro-buret appears to have leaked, resulting in calculated oxygens that were too high; the deep cast oxygens on station 10 were lost.

Silicate, phosphate, nitrate and nitrite nutrients were determined at sea using an automated analyzer. The procedures used are similar to those described by Atlas et al. (1971). There were some problems in both the phosphate and nitrate analyses. A batch of artificial seawater used for standards on leg II was contaminated and resulted in inaccurate phosphate factors. Also, a change in cadmium reduction columns (at station 103) used in the nitrate analyses resulted in inconsistent nitrate reduction efficiency for several stations; nitrates were lost on three stations. On several other stations, phosphate and/or nitrate was re-calculated on the basis of typical cruise NO_3/PO_4 ratios. Most changes were less than 6%. Nitrite was not run on four stations because the colorimeter was used for another analyses. Nitrate could not be corrected for the presence of nitrite on those stations, so the results are listed as measured, $NO_3 + NO_2$.

CONDUCTIVITY/TEMPERATURE/DEPTH (CTD) DATA

Only the deep cast CTD lowering on each station was processed by PACODF. They provided tapes of the CTD temperature and salinity data at one-decibar intervals, usually for the down cast. At times, there were problems with the down cast and the up cast data are given instead. The oxygen probe data were not processed. The quality of the CTD data was degraded on some stations because of electrical noise from one of three different sources: the winch slip rings, the end cable termination and loose bulk head connectors to the CTD. At times the specific problem was quickly identified and fixed at sea, and at other times the problem persisted for several stations. The problem stations are readily apparent from inspection of the individual CTD station curves shown in the latter part of this report. The CTD data have been filtered somewhat, but no attempt has been made to improve the noisier stations. Some loss of CTD data is also apparent in the CTD plots in high gradient regions; the gradient filter used in processing the CTD data appears to have been too severe. After removal of some surface spikes and a few large spikes near 1000 db, standard depth data were extracted from the one-db interval tapes and are listed in this data report. The complete one-db interval tapes are available from NODC.

TABULATED DATA

The time given is the Greenwich Mean Time of the first bottle trip. For CTD casts, it is the start down time for down casts or the start up time for up casts.

Station positions were derived from satellite fixes closest to, or bracketing the cast time.

Bottom depths, determined acoustically, have been corrected using British Admiralty Tables (Carter, 1980). The bottom soundings were taken at the time that the rosette was near the bottom.

Wind and wave directions are given to the nearest to degrees. Wind speed is given in knots and the wave height and period are given in feet and seconds, respectively.

Weather conditions are coded using WMO code 4501 (Table 2).

Barometer and air temperature are shown in millibars and degrees Celsius.

The dominant cloud type is given in the standard two-letter code and the cloud amount is recorded in octos.

Observed hydrographic data and interpolated standard level data have been interspersed and are presented together in depth sequence. Interpolated or extrapolated data are indicated by the footnote letters "ISL" listed after the depth.

Potential temperatures have been calculated from the expressions given by Fofonoff (1977), based upon Bryden's (1973) results.

Density-related parameters are calculated from the International Equation of State of Seawater, 1980 (UNESCO, 1981). Sigma-theta, sigma-2 and sigma-4 are the density anomalies for the sample moved adiabatically to the surface, 2000 db and 4000 db using Fofonoff's (1977) procedure. SVA is the specific volume anomaly.

Percent oxygen saturation was calculated from the equations of Weiss (1970).

FOOTNOTES

In addition to footnotes, special notations are used without footnotes because the meaning is always the same.

ISL: After depth values indicates interpolated or extrapolated standard level.
D: CTD value listed in place of normal ship-board hydrographic measurement.
H: Ship-board hydrographic measurement listed in place of normal CTD values.

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TABLE 1: Ancillary Sampling on AJAX Expedition

Measurement:	Investigator:
Underway pCO_2, pCH_4, pN_2O	R.F. Weiss, SIO
Chlorofluoromethanes	R.F. Weiss, SIO
Tritium	W.J. Jenkins, WHOI
3He	W.J. Jenkins, WHOI
Alkalinity, CO_2, pCO_2	T. Takahashi, LDGO
	D. Chipman, LDGO
Pb	E. Boyle, MIT
Trace Metals	E. Boyle, MIT
	K. Bruland, UCSC
	J. Edmond, MIT
Rare Earths	G. Wasserburg, CIT
	D. Pipegras, CIT
Nd Isotopes	G. Wasserburg, CIT
	D. Pipegras, CIT
Pb-21O	K. Turekian, Yale
Surface Ra-228/226	W. Moore, USC
Photosynthetic Pigments	J.M. Brooks, TAMU

TABLE 2: WMO Weather Code 4501

Code:	
0	Clear (no cloud at any level)
1	Partly cloudy (clouds scattered or broken)
2	Continuous layer(s) of c1oud(s)
3	Sandstorm, dust storm, or blowing snow
4	Fog, thick dust, or haze
5	Drizzle
6	Rain
7	Snow, or rain and snow mixed
8	Shower(s)
9	Thunderstorm(s)

AJAX LEG I PERSONNEL

SHIP'S CAPTAIN

Casiles, David F., R/V *Knorr*

PERSONNEL PARTICIPATING IN THE COLLECTION OF DATA

Reid, Joseph L.	Chief Scientist, Professor, SIO
Beaupre, Marie-Claude	Staff Research Associate, SIO
Chipman, David W.	Research Associate, LDGO
Conway, Carol B.	Staff Research Associate, SIO
Costello, James P.	Staff Research Associate, SIO
Field, Timothy J.	Marine Technician, SIO
Mantyla, Arnold W.	Specialist in Oceanography, SIO
Mattson, Carl W.	Electronics Technician, SIO
Muus, David A.	Staff Research Associate, SIO
Shen, Glen T.	Graduate Research Assistant, MIT
Van Woy, Frederick A.	Staff Research Associate, SIO
Warner, Mark J.	Research Assistant, SIO
Wells, James A.	Marine Technician, SIO

AJAX LEG II PERSONNEL

SHIP'S CAPTAIN

Bowan, Richard, R/V *Knorr*

PERSONNEL PARTICIPATING IN THE COLLECTION OF DATA

|	
Nowlin, Worth D., Jr.	Chief Scientist, Professor, TAMU
Bidigare, Robert R.	Assistant Research Scientist, TAMU
Bos, David L.	Staff Research Associate, SIO
Bullister, John L.	Research Assistant, SIO
Chipman, David W.	Research Associate, LDGO
Conway, Carol B.	Staff Research Associate, SIO
Costello, James P.	Staff Research Associate, SIO
Field, Timothy J.	Marine Technician, SIO
Frank, Tamara	Graduate Research Assistant, TAMU
Richter, Walter A.	Electronics Technician, SIO
Rintoul, Stephen R.	Graduate Research Assistant, WHOI/MIT
Trull, Thomas W.	Graduate Research Assistant, WHOI/MIT
Van Woy, Frederick A.	Research Associate, SIO
Wells, James A.	Marine Technician, SIO
Whitworth, Thomas, III	Associate Research Scientist, TAMU
Williams, Robert T.	Principle ADP Systems Analyst, SIO
Worley, Steven J.	Research Associate, TAMU
Zastrow, Colleen E.	Graduate Research Assistant, TAMU
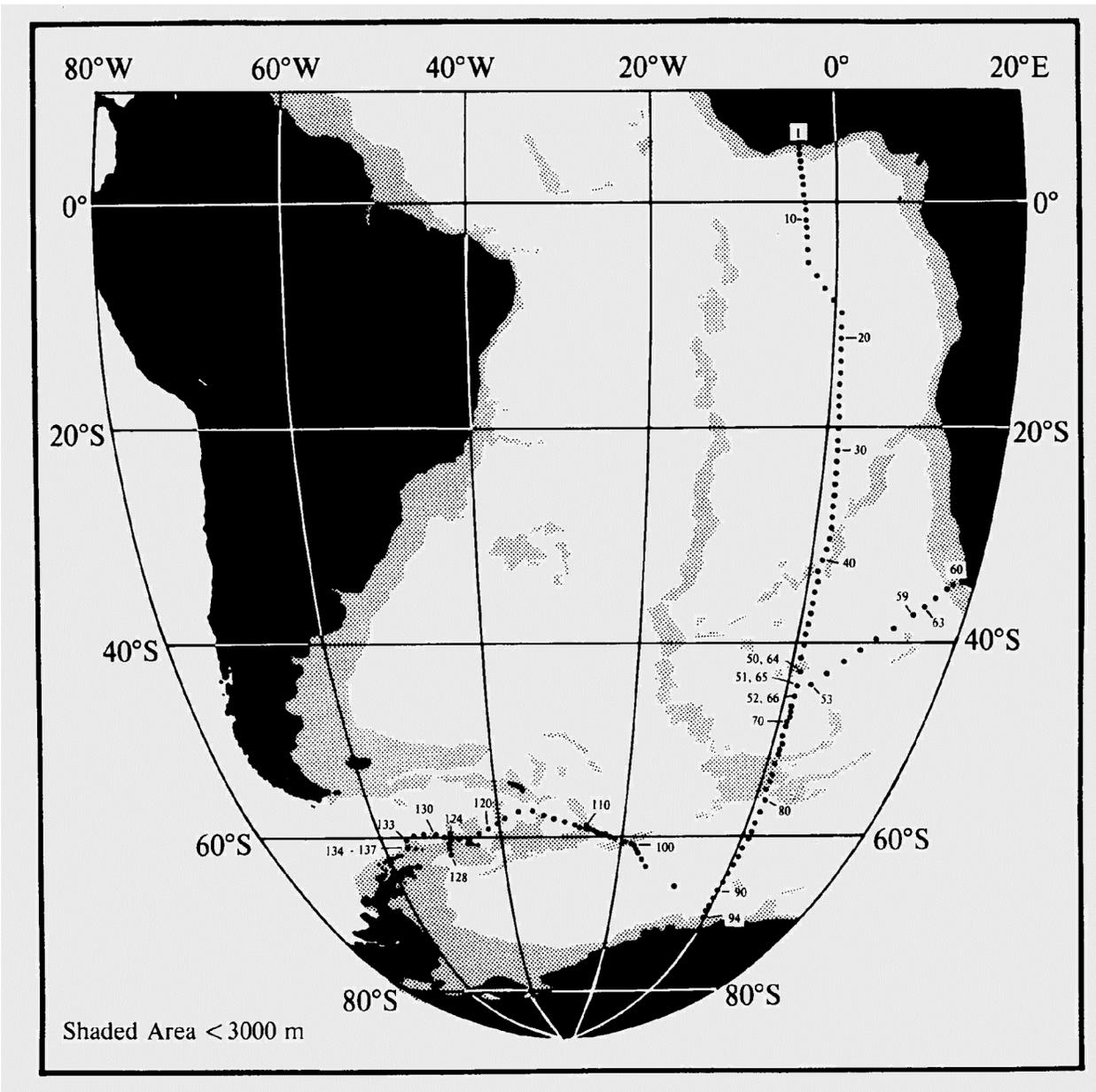
Figure 1: *AJAX Expedition Station Positions*

Carbon Chemistry of the South Atlantic Ocean and the Weddell Sea

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Lamont-Doherty Geological Observatory
December, 1986

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_2 (pCO_2) and the concentration of total dissolved carbon dioxide (total CO_2 or TCO_2) 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 analyzed for TCO_2 in our land-based laboratory using the new technique of CO_2 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_2, TCO_2, 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_2, TCO_2, TALK, and apparent oxygen utilization (AOU) along the Greenwich meridian from 50°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).

EXPERIMENTAL METHODS

Gas Chromatograph System for pCO₂ Analysis

The equilibrator-gas chromatograph system used during the expedition for the determination of partial pressure of CO_2 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 pCO₂, 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.
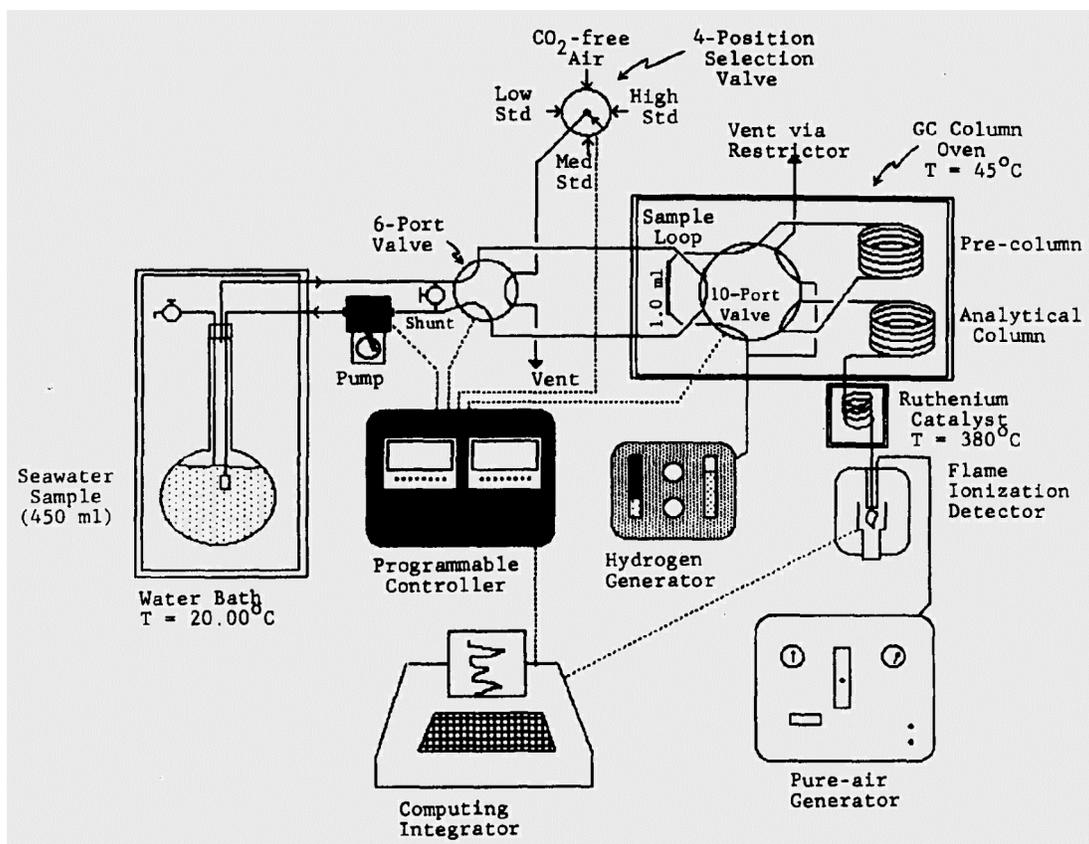

Figure 1: *Schematic diagram of gas chromatograph-based system for the determination of CO₂ partial pressure in seawater. Single solid lines represent gas flow pathways, dotted lines represent data and control signal paths, and solid double lines enclose thermally isolated zones. The valves are shown 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 CO₂ peak elutes from the precolumn into the analytical column, the 10-port valve will be returned to its normal position, backflusing 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.

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 with air of known CO_2 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 end 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_2 from the other components of the air. After separation, the CO_2 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 ±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_2 peak is computed, and the concentration of CO_2 in the sample is determined by comparison with the peak areas of known amounts of CO_2 from reference gas mixtures. The GC detector response is calibrated at least once per hour by injecting, with the same sample loop, CO_2–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_2 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_2 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 ± 0.3 millibars, calibration traceable to NBS provided by manufacturer). Additional corrections are required to account for the change in pCO_2 of the sample water due to the transfer of CO_2 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_2 measurement is estimated to be about ± 0.2%.

GC and Coulometric Systems for Total CO_2 Measurements

Two independent methods were used for the measurement of total CO_2 (TCO_2) in seawater: determination at sea using the gas chromatograph described above with a separate CO_2–extraction subsystem, and that in the shore–based laboratory of stored water samples using the new technique of CO–cou1ometry. Both techniques will be described below.

The gas-chromatograph system used on board the ship consisted of an extraction system for removing the CO_2 from acidified 3-ml water samples linked to the same gas chromatograph that was used for the 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 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 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 (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 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 CO_2 in the system remains dissolved in the acidified water. The maximum temperature variation due to changes in room temperature, 4°C, would cause a variation in the fraction of the CO_2 in the water of approximately 10% of the amount retained, or about 2 umol/kg. The maxima 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 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 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 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, 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, transfer-ring the water to an extraction tube, acidifying, and sweeping the evolved CO_2 into the cell of a CO_2 coulometer with a flow of CO_2−free carrier gas. In the coulometer cell, the CO_2 is quantitatively absorbed by a solution of ethanolamine in dimethylsulfoxide (DMSO). Reaction of the CO_2 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 hydoxyl ($OH−$) ions from a small amount of water in the solution. The $OH−$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 $OH−$generated to titrate the acid and hence to the number of moles of CO_2 absorbed to form the acid.
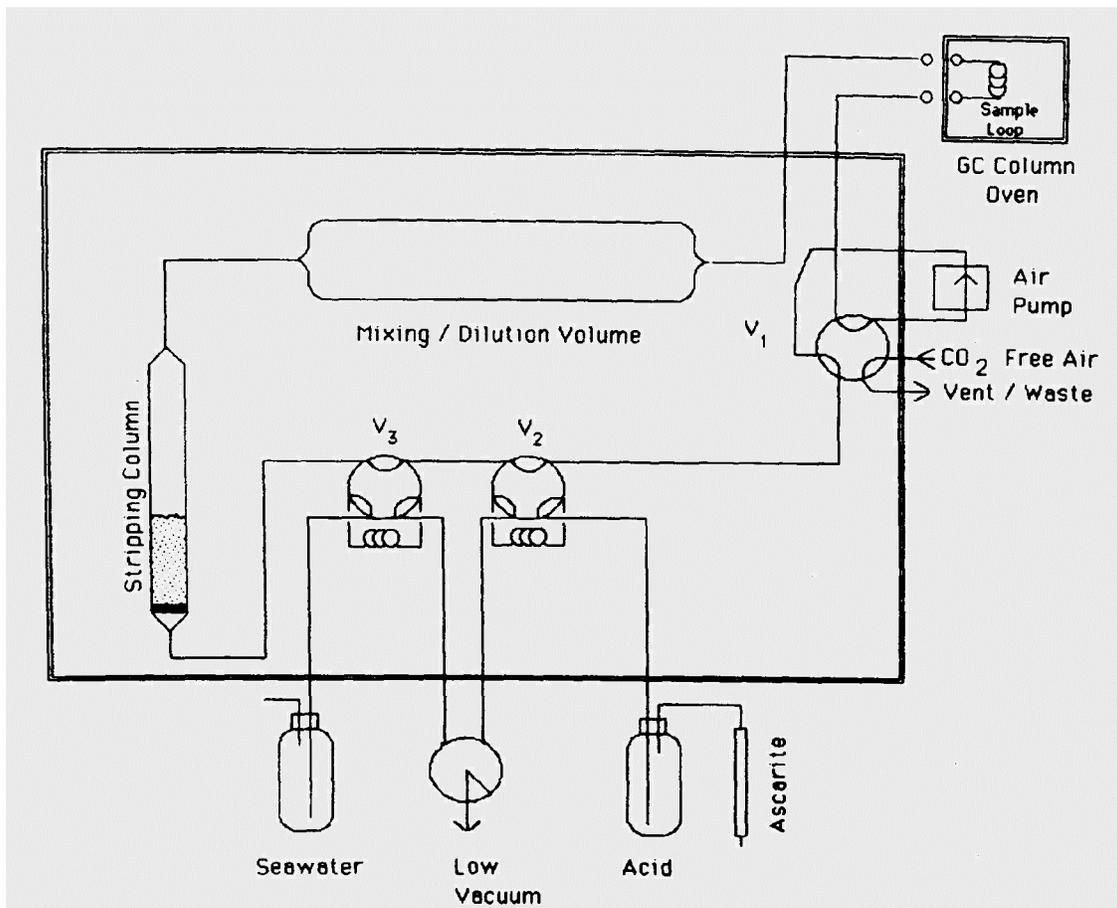
Figure 2: *Schematic diagram of the CO_2 extraction subsystem of the gas chromatograph TCO_2 analysis system. In operation, the lines shown connected to the CC sample loop are attached to the 10-port valve shown in Figure 1, in place of the pCO_2, equilibration subsystem. The valves on Figure 2 are shown in the position they would have while CO_2 is being stripped from the acidified seawater sample. Valves V2 and V3, which allow the introduction of metered quantities of hydrochloric acid and seawater respectively, have been returned to the fill position to allow for the preparation of the next sample. After cycling the 10-port valve (Figure 1) to inject an aliquot of CO_2-air mixture for analysis, V1 will be turned to alternate position, which will cause CO_2-free air to sweep the system of CO_2 and force the stripped acidified water in the stripping-column out through V1 by way of V2 and V3 to a waste reservoir.*

We have calibrated the coulometer in four different ways: by injecting measured volumes of pure CO_2 gas at known pressure and temperature, by analysis of the CO_2 evolved from gravimetrically prepared solid calcium carbonate and sodium carbonate, and by injecting measured volumes of CO_2–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_2 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 ± 1 uM/liter in samples of 2200 uM/liter.

Atmospheric CO_2 measurements

Air samples were analyzed for CO_2 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_2 in the sample to be computed directly. Table 1 lists the concentration of CO_2 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_2 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_2 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_2 observed during the two legs of AJAX cruise. Samples were analyzed without removal of water vapor, and the concentration in dry air (VCO_2) have been computed using the observed wet and dry bulb thermometer readings. The CO_2 concentration in air saturated with water vapor at the temperature of the sea surface (VCO_2^*), and the partial pressure of CO_2 in water–saturated air (pCO_2) at the barometric pressure which was observed at the of analysis (pCO_2) are also given.

DATE	TIME (GMT)	LAT	LONG (DEG MIN)	VCO2	VCO2* (ppm)	PRESS (mb)	pCO2 (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 5	55 38.6 W	342	340	993.9	334

CALIBRATION AND DATA REDUCTION METHODS

The methods used to calculate pCO_2 or 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 pCO_2 of the air in the sample loop to be determined from the CO_2 peak area; 2) for TCO_2, the relative volumes of the water sample loop, air sample loop and CO_2–extraction system are determined by measurement of the CO_2 evolved from samples of gravimetrically prepared sodium carbonate solution; and 3) also for TCO_2 measurements, a correction for the extraction efficiency of the stripping system was applied using the comparison between the TCO_2 measured with the GC and that measured with 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 TCO_2 analyses, while pCO_2 measurements were calculated from a response curve which was parabolic and passed through the values of all three standard gas mixtures (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 Figure 3a, 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 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 uM/kg) for all, samples. As shown in Figure 3b, 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 pCO_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 l at 1600 ppm) do not apply. Only the central portion of the figure, representing the range of 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 uM/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 l% during the interval between successive calibration sequences (less than one hour). Rapid changes in the shipboard laboratory temperature were experienced as the outside door 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.
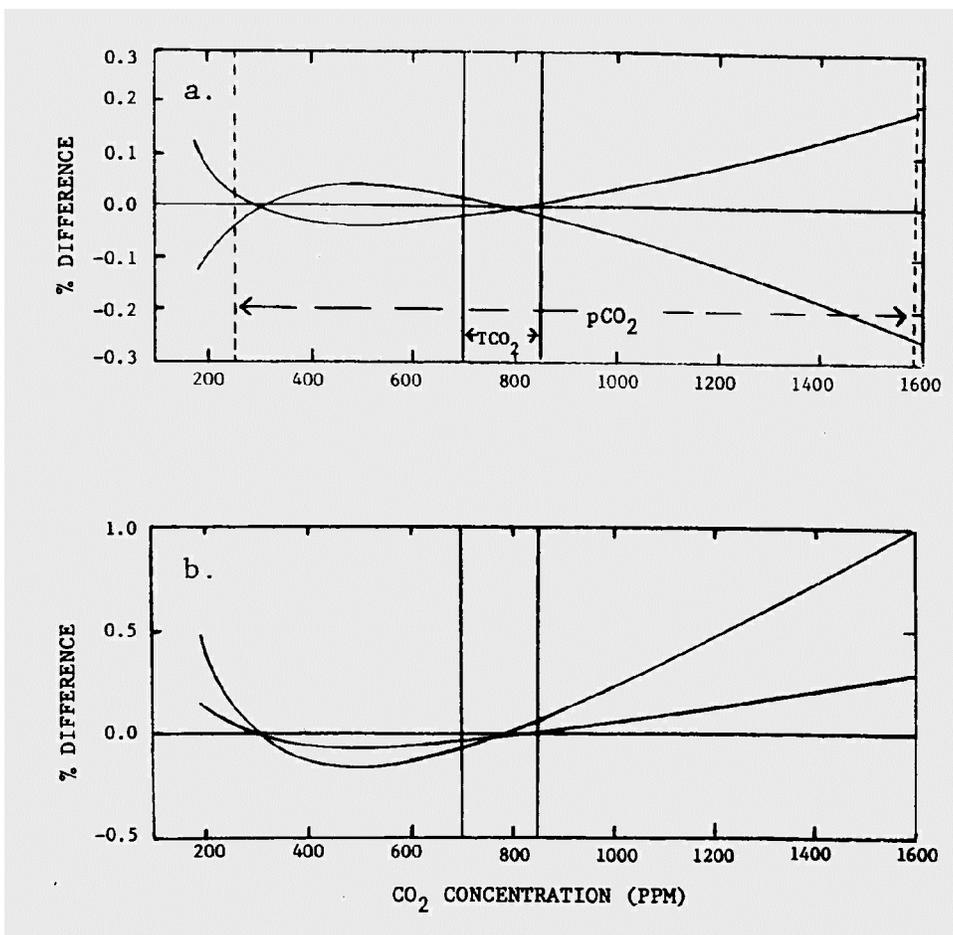
Figure 3: *The difference between the CO_2 concentrations estimated using assumed linear and parabolic detector responses. The zero reference line represents a linear fit to two calibration points, and the curved lines represent the upper and lower limits of parabolic fits to three calibration points,*

a.) *This panel applies to the measurements during Leg 1. The vertical dashed and solid lines indicate the ranges of measured pCO_2 and 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 TCO_2 and less than 0.2% for 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 pCO_2 measurements during Leg II, parabolic fits to three calibration points were used. For the TCO_2 measurements demarked by solid vertical lines, linear fits to two calibration points were used.*

Calibration of TCO$_2$ extraction system

The number of moles of CO_2 in the GC sample loop at the time of injection of a TCO$_2$ 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_2 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 submersed 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_2 concentration to establish the relationship between CO_2 concentration of the sample and the number of moles of CO_2 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_2 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_2 water. During Leg 1, this water was prepared by stripping distilled water with CO_2–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_2 was checked by running an aliquot as an unknown, and the final concentration of CO_2 in the standard solutions was corrected for this residual CO_2 . 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$_2$ 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_2 in the recirculating gas was slightly low. This effect was not noticed during the cruise, but became evident when the TCO$_2$ 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. ±0.9 uM/kg, as shown in Figure 5). Thirdly, our long–term sample storage tests

show that the total CO_2 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_2 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%, end in general the correction was less than 0.3%.

Figure 4 shows a comparison of the coulometer TCO_2 data with the GC TCO_2 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 ± 5.4 uM/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 ± 3 uM/kg (root mean square deviation).

COMPARISON WITH THE RESULTS OF OTHER EXPEDITIONS

Figure 5 shows a plot of TCO_2 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_2 values, as determined using the potentiometric alkalinity titrator, have been plotted as originally reported. However, a recent comparison of the GEOSECS TCO_2 measurements in the North Atlantic with those computed from the alkalinity and pCO_2 measurements made at the same location during the TTO/North Atlantic Study indicates that the Atlantic GEOSECS 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 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 uM/kg). The WWSP TCO_2 values were obtained recently using shipboard 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 ±0.9 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 ± 3.7 uM/kg) gives confidence that the correction applied to the GEOSECS data is indeed justified. The stored 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 ± 2.8 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 ± 3.0 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 ± 3.4 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 uM/kg, and consequently the agreement with the other data sets is meaningful.
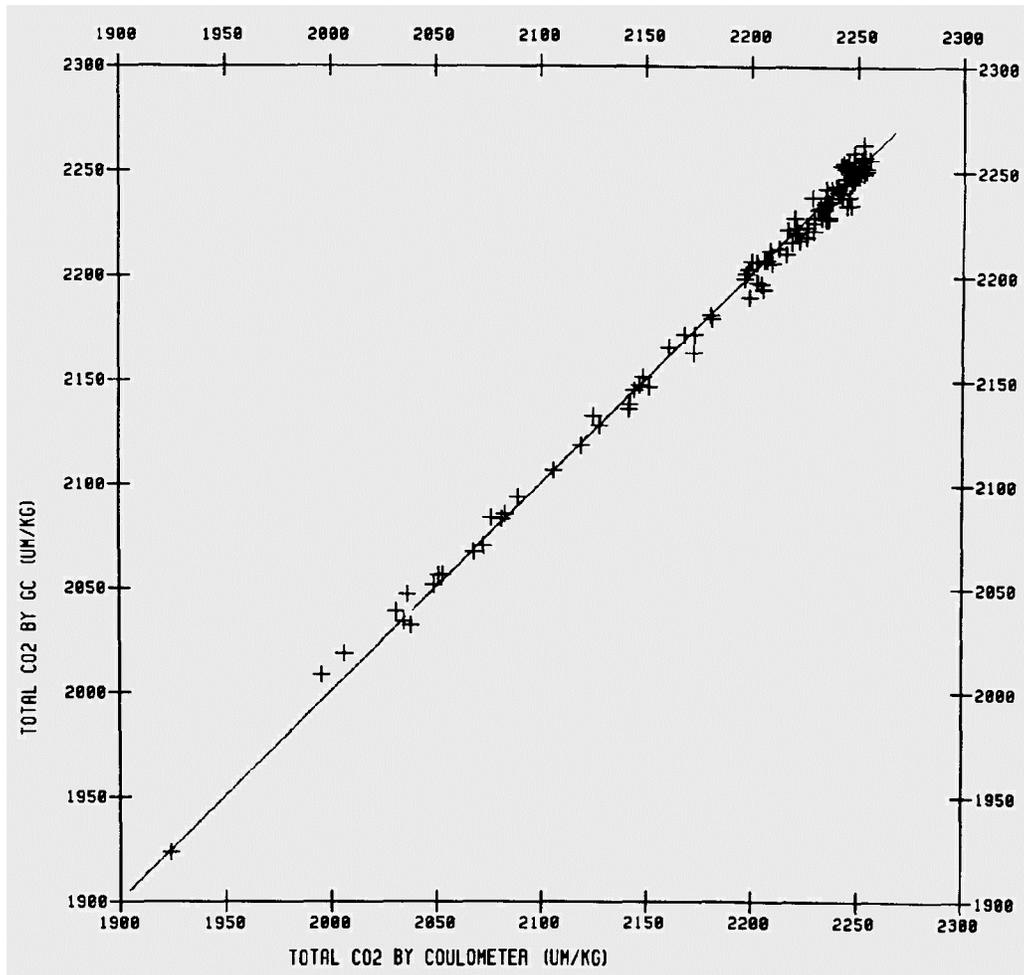
Figure 4: *Comparison of the values of total CO_2 concentration (TCO_2) determined on duplicate pairs of samples by means of gas chromatography (CC) and shore–based coulometry. The coulometric measurements have been used to provide the over–all calibration of the GC–based system; consequently the points 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 uM/kg) is attributed to random errors in the GC–based measurements.*
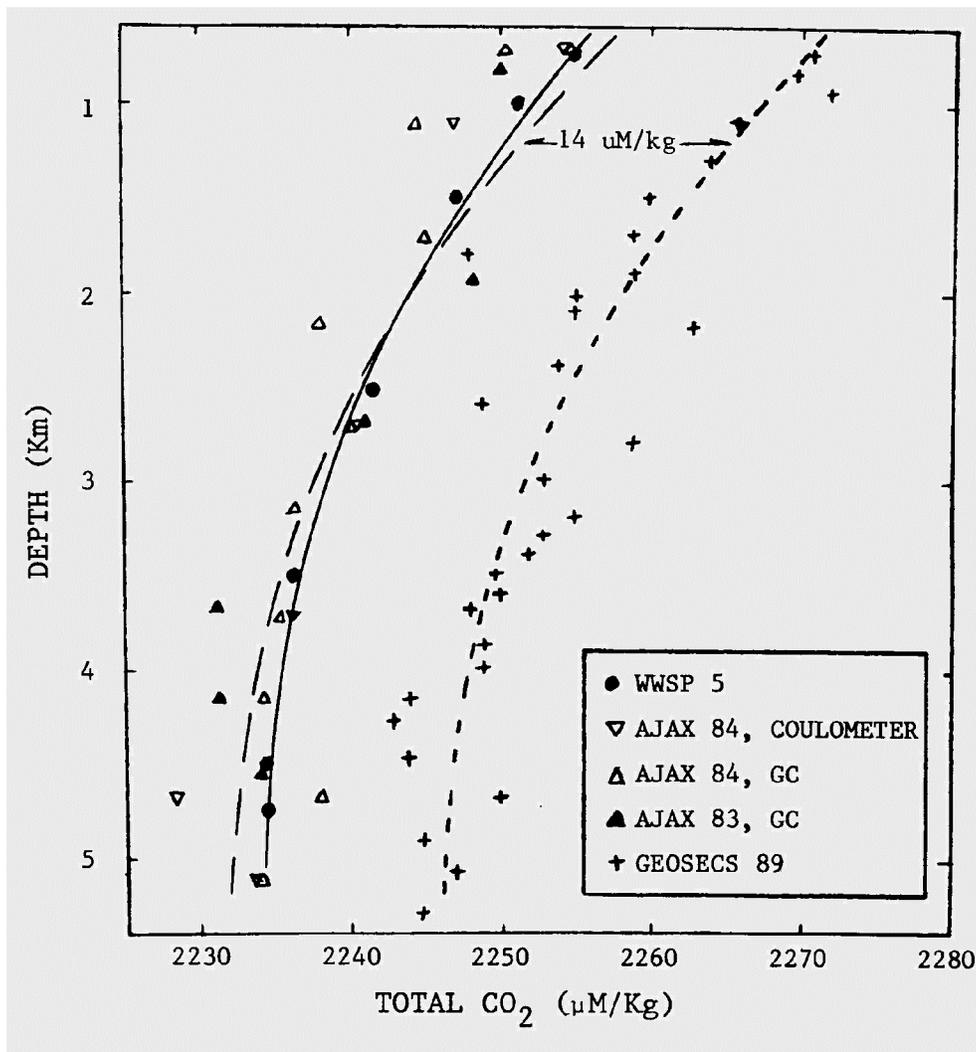
Figure 5: *Comparison of the total CO2 concentration data obtained at GEOSECS Station 89, Winter Weddell Sea Project (WWSP) Station 5 and Long Lines (AJAX Station 83 and 84. These stations are located at about 60°S and 1°E. The GEOSECS data (+) were obtained by means of a potentiometirc titration method; the WWSP data (•) :were obtained by means of a coulometric method; and the AJAX data were obtained by means of GC (△ and ▲) and coulometric (▽) 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 uM/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 uM/kg. When the GEOSECS data are corrected by -14 uM/kg as suggested by Takahashi et al. (1986), the corrected values are consistent with the WWSP data as indicated by the long-dashed curve.*

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Takahashi, T., D. Chipman, N. Schechtman, J. Goddard and R. Wanninkhof, 1982, Measurements of the partial pressure of CO_2 in discrete water samples during the North Atlantic Expedition, the Transient Tracers of Ocean Project. Technical Report, Lamont-Doherty Geol. Obs., Palisades, N.Y., 268 pp.

Takahashi, T., W.S. Broecker and S. Langer, 1985, Redfield ratio based on chemical data from isopycnal surfaces. *Jour. Geophys Res.*, 6907-6924.

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SECTION II MERIDIONAL PROFILES OF CARBON CHEMISTRY AND APPARENT OXYGEN UTILIZATION ALONG THE PRIME MERIDIAN, 4°N – 70°S

Figure 6: *Station locations for the Long Lines (AJAX) Expedition.*
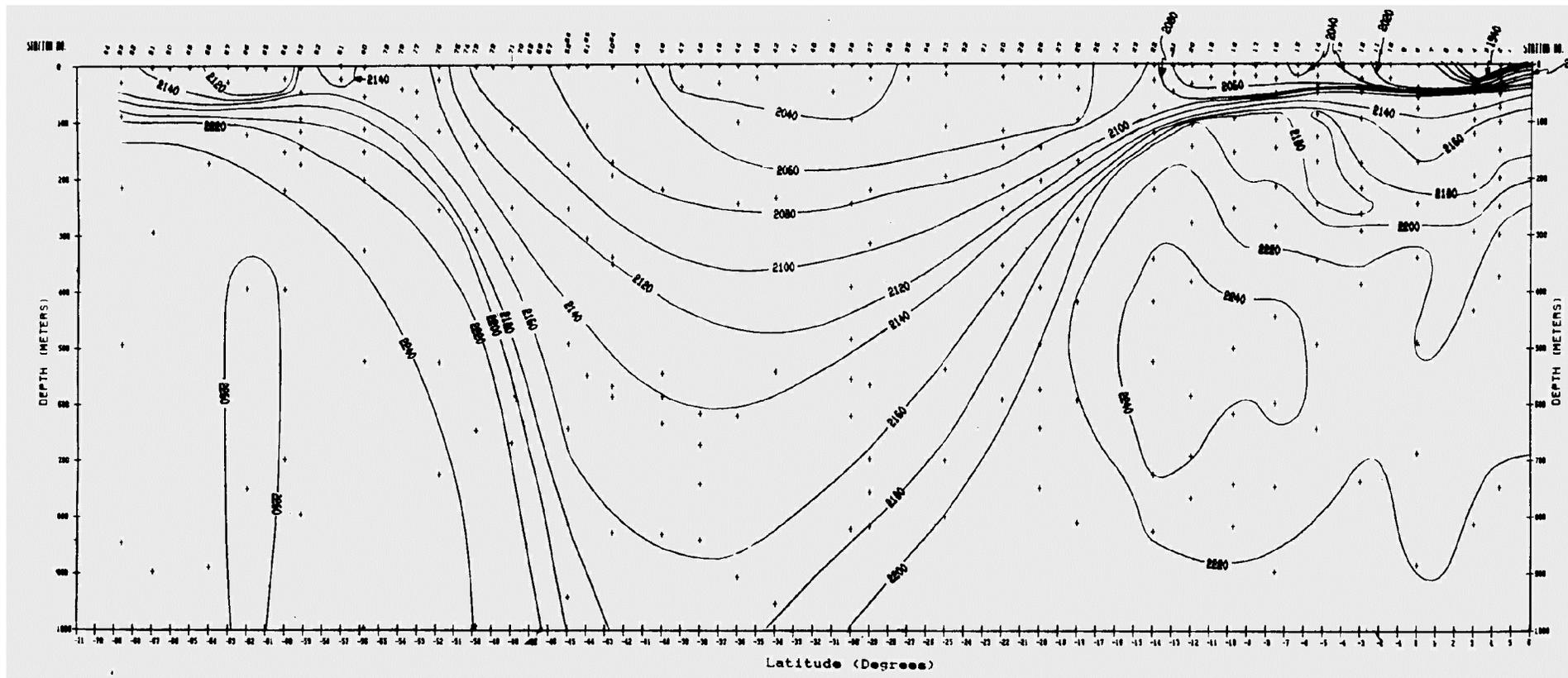
Figure 7a: *Meridional distribution of the total CO₂ concentration (uM/kg) in seawater along the prime meridian, 0 - 1000 meters.*
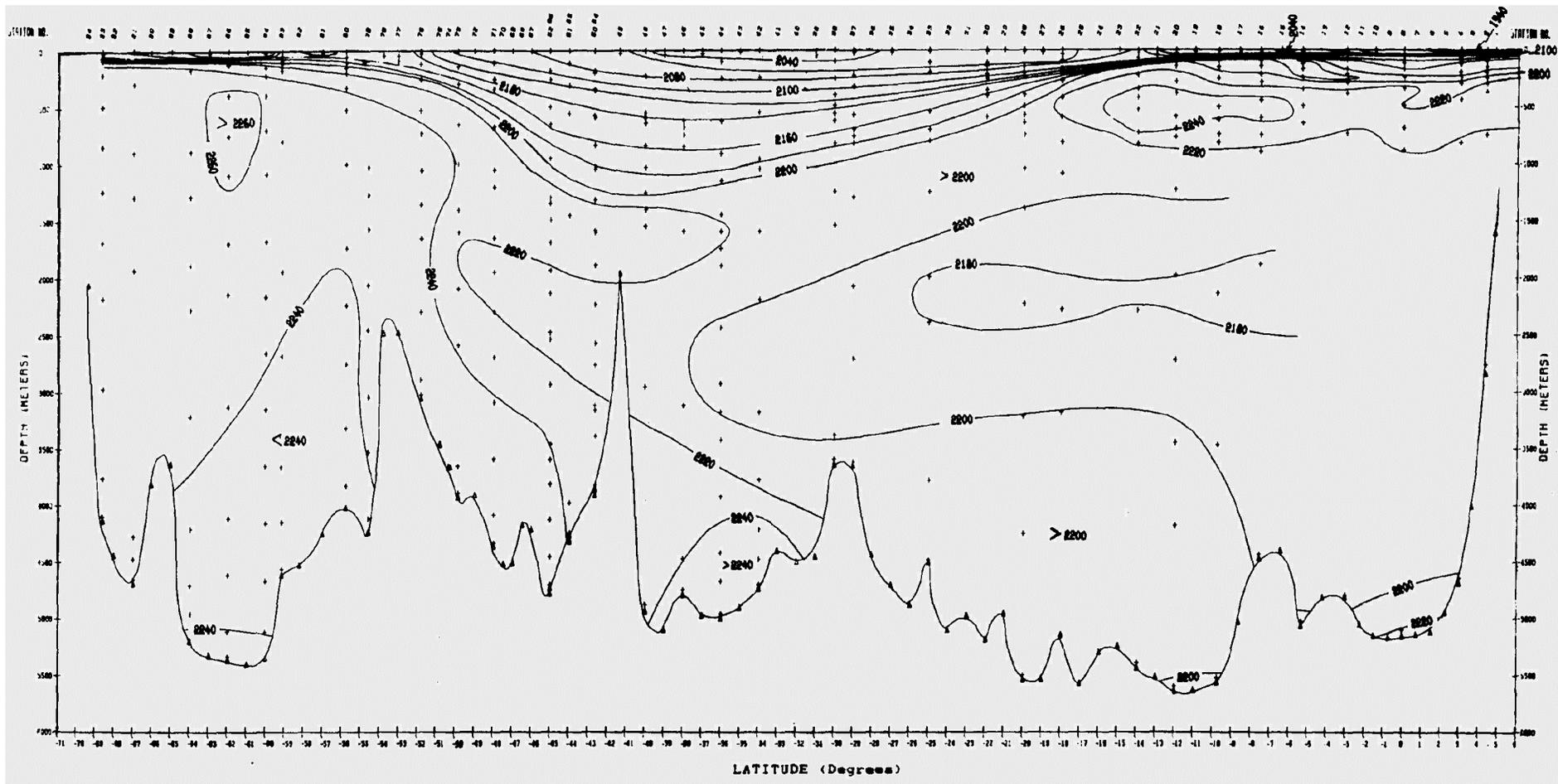
Figure 7b: *Meridional distribution of the total CO₂ concentration (uM/kg) in seawater along the prime meridian, 0 - 6000 meters.*
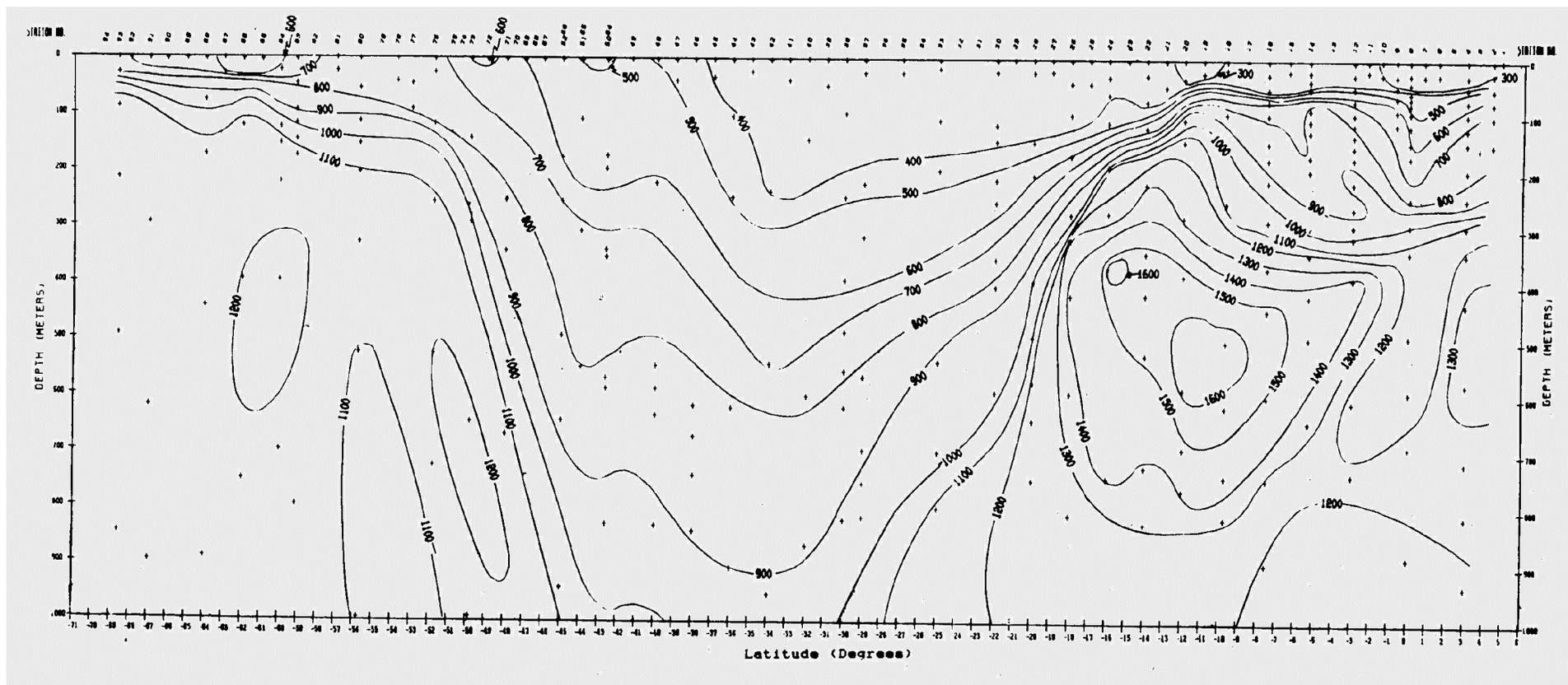
Figure 8a: *Meridional distribution along the prime meridian of pCO₂ (uatm) in seawater at 20°C, 0 - 1000 meters.*
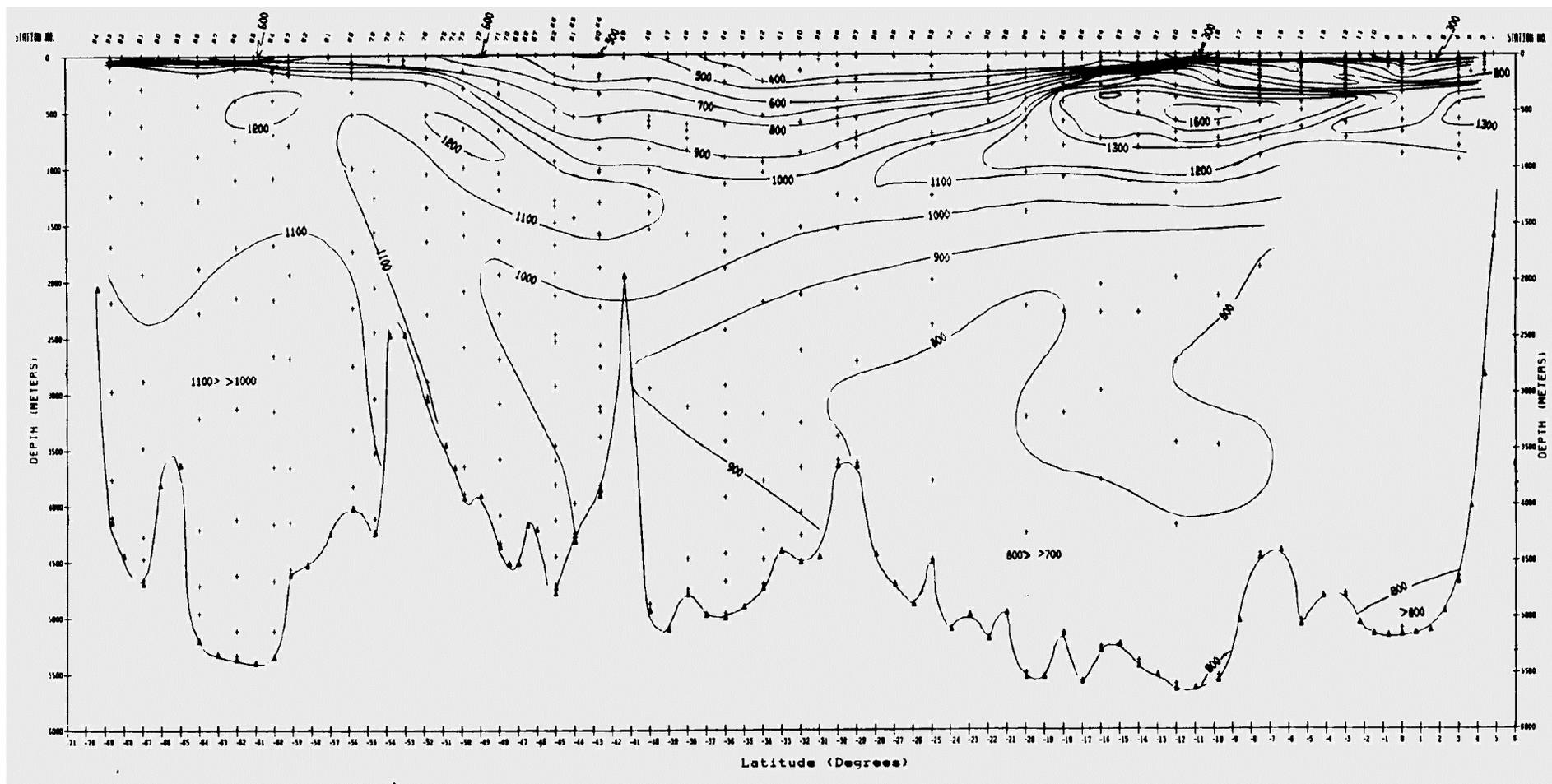
Figure 8b: *Meridional distribution along the prime meridian of pCO₂ (uatm) in seawater at 20°c, 0 - 6000 meters.*
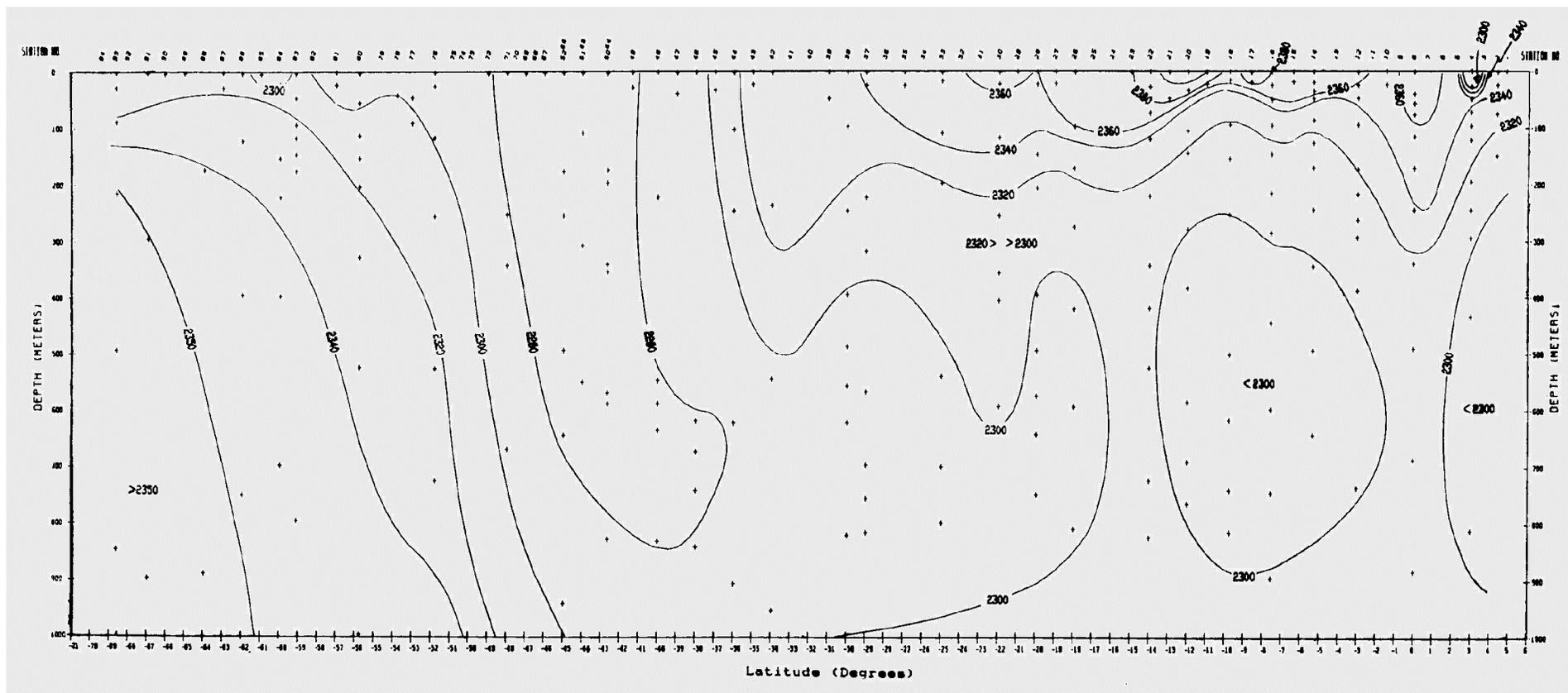
Figure 9a: *Meridional distribution along the prime meridian of the total alkalinity (ueq/kg) in seawater, 0 - 1000 meters.*
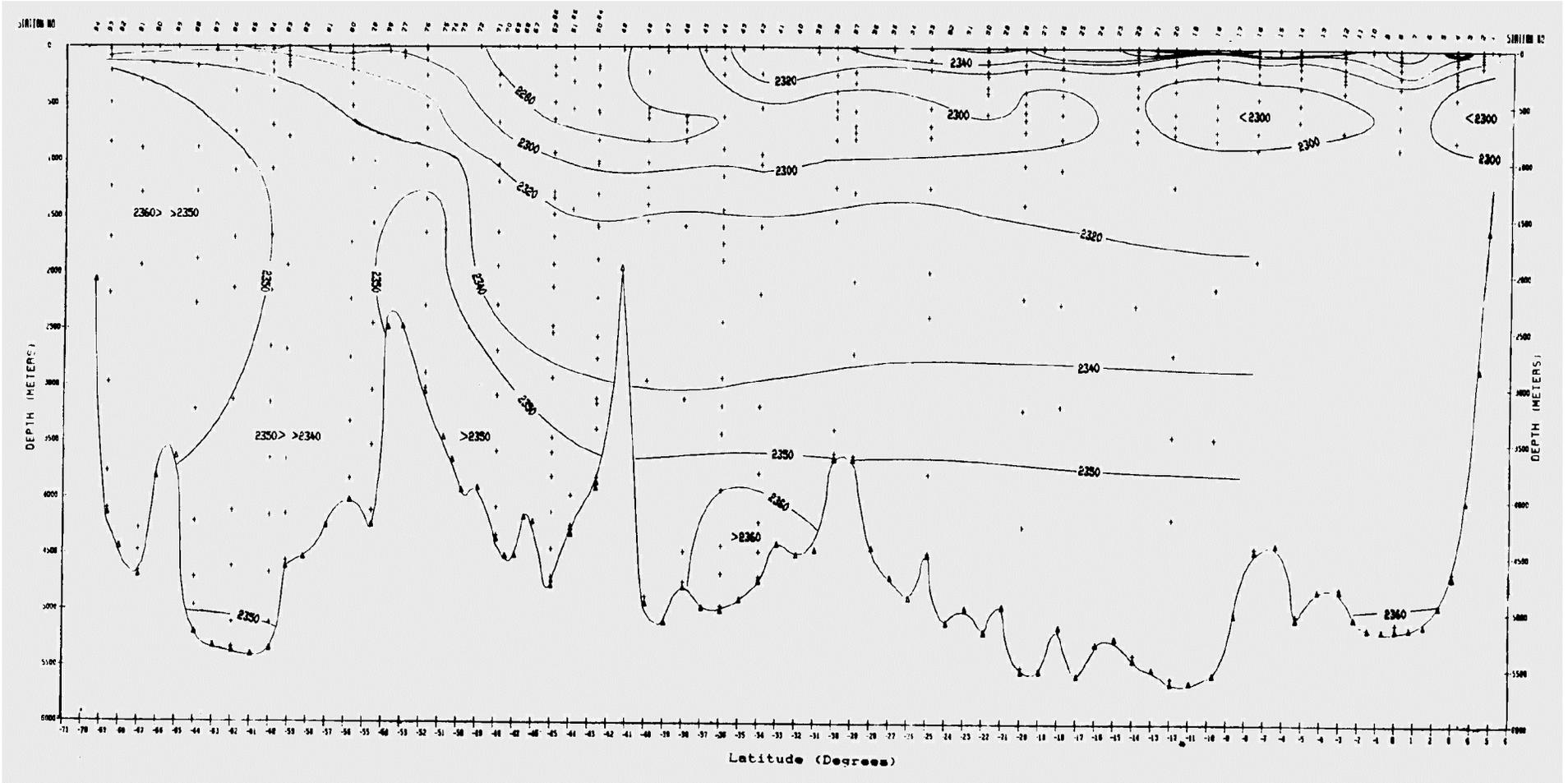
Figure 9b: *Meridional distribution along the prime meridian of the total alkalinity (ueq/kg) in seawater, 0 - 6000 meters.*
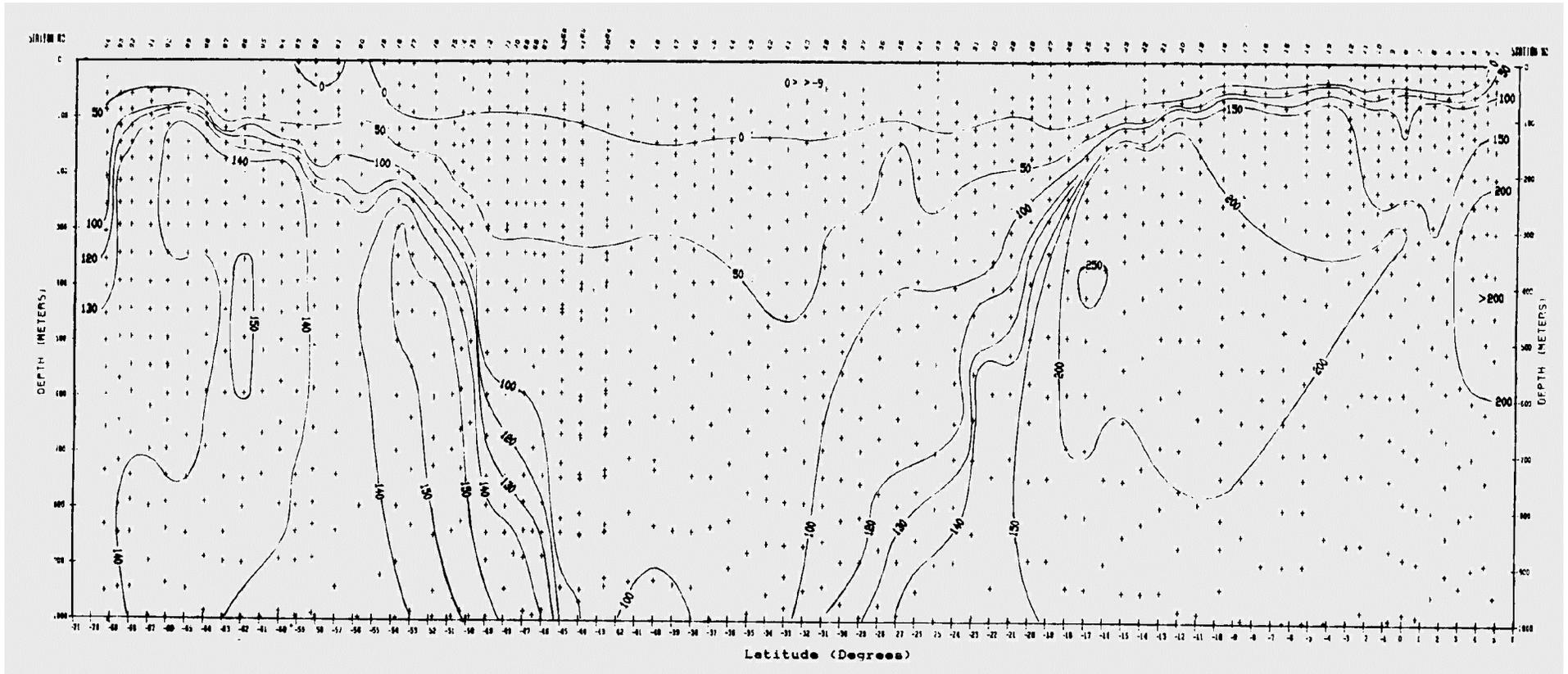
Figure 10a: *Meridional distribution along the prime meridian of the apparent oxygen utilization, AOU, in seawater (uM/kg), 0 - 1000 meters.*
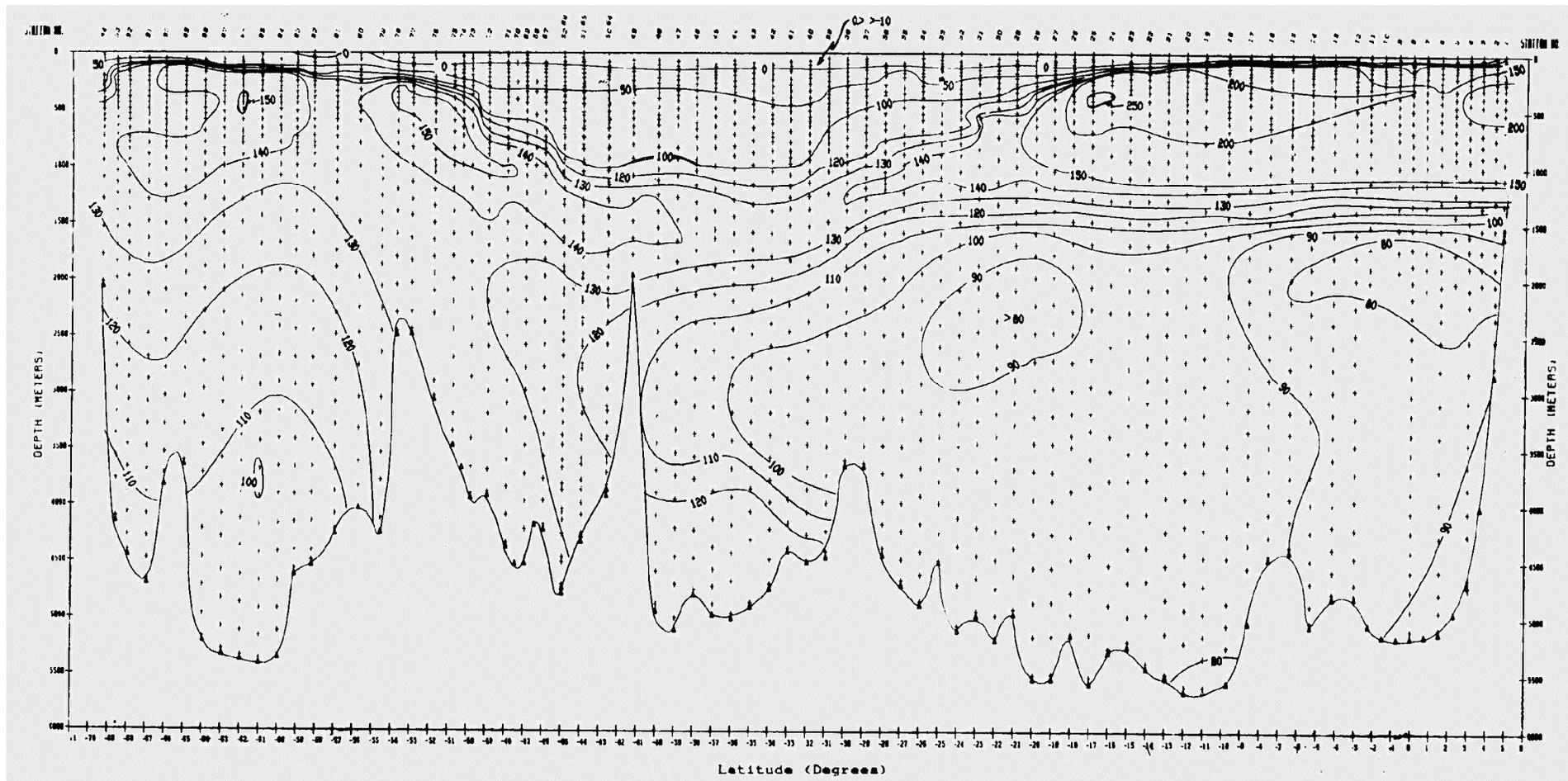
Figure 10b: *Meridional distribution along the prime meridian of the apparent oxygen utilization, AOU, in seawater (uM/kg), 0 - 6000 meters.*

SECTION III PROPERTY–PROPERTY RELATIONSHIPS OF THE LONG LINES DATA

Figure 11: *Potential temperature versus salinity*
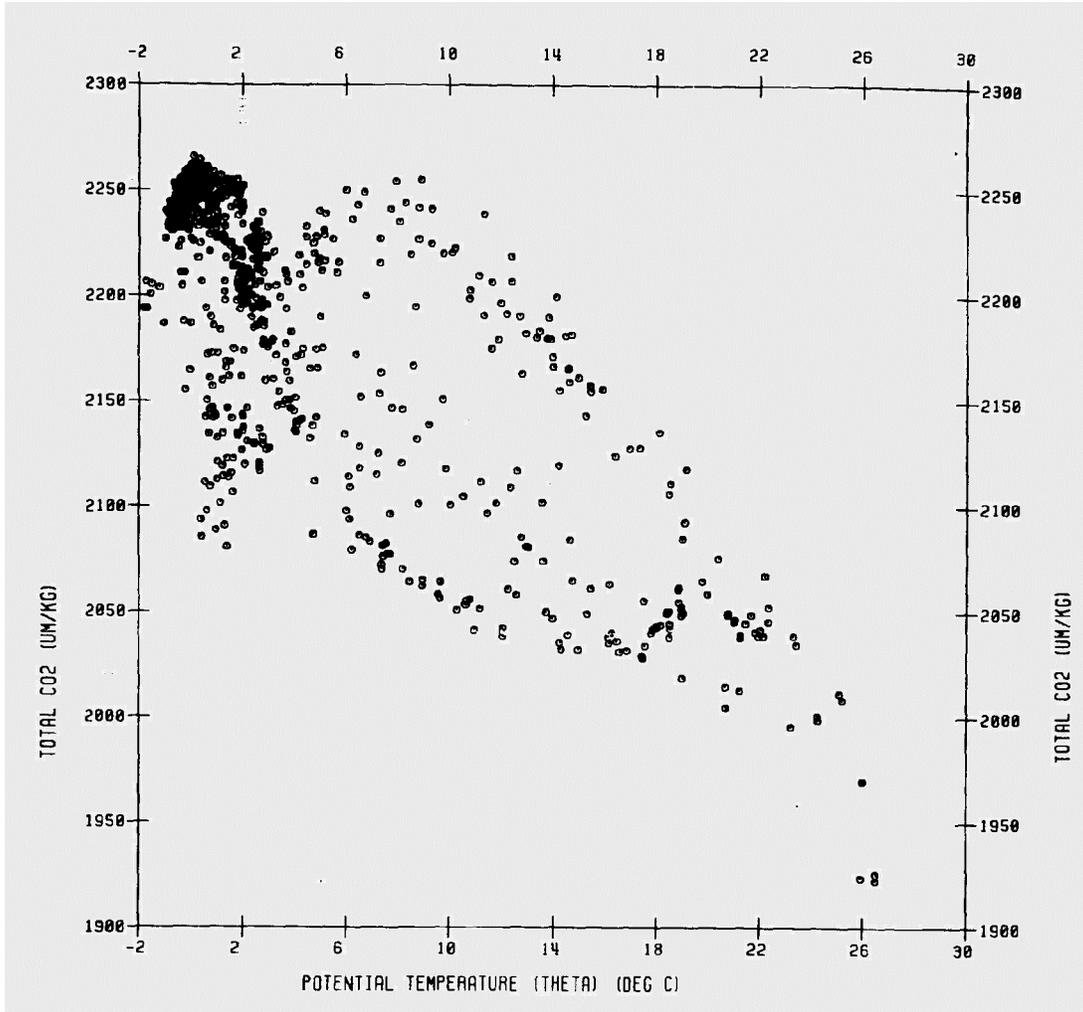
Figure 12: *Total CO₂ concentration versus potential temperature*
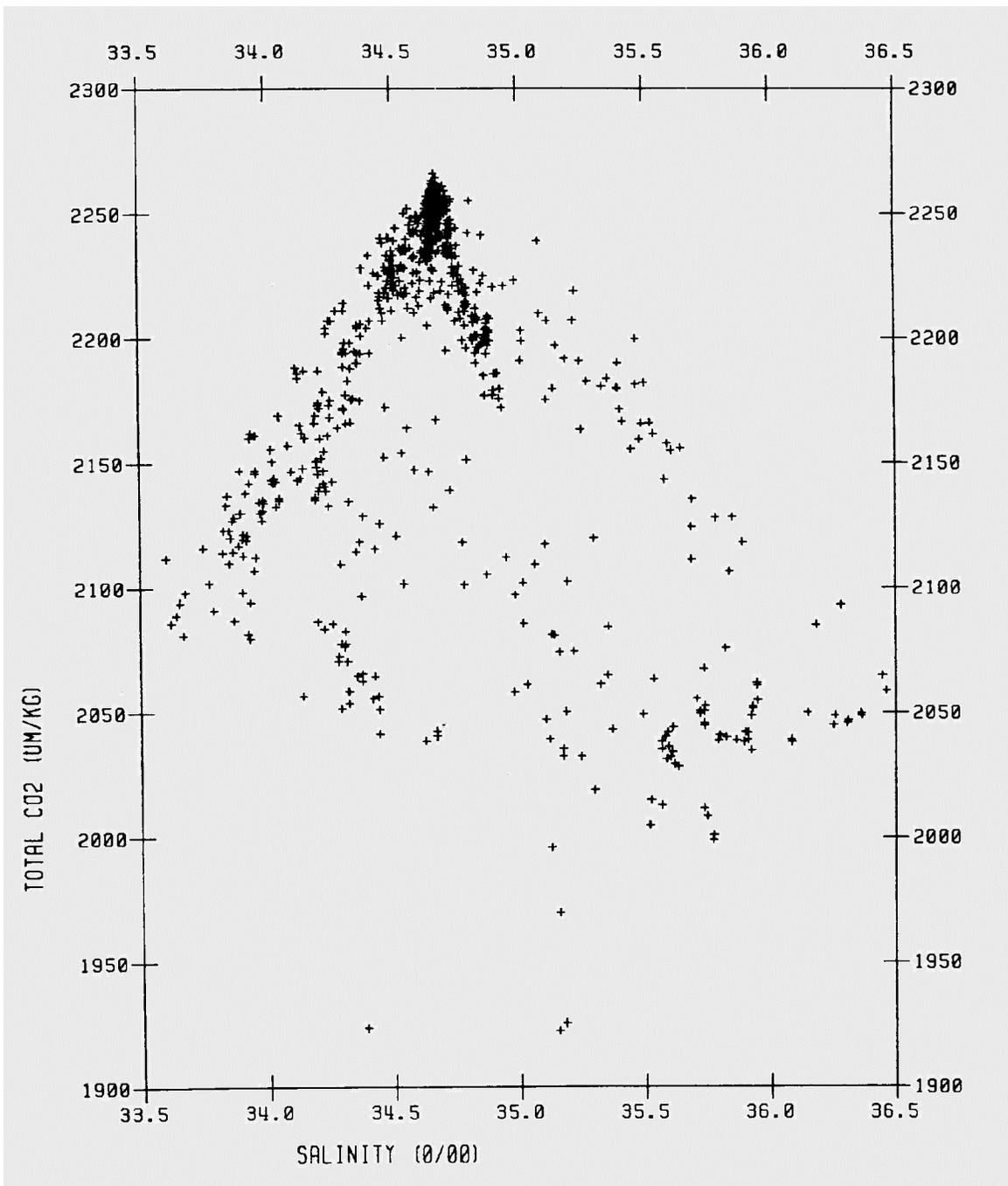
Figure 13: *Total CO2 concentration versus salinity*
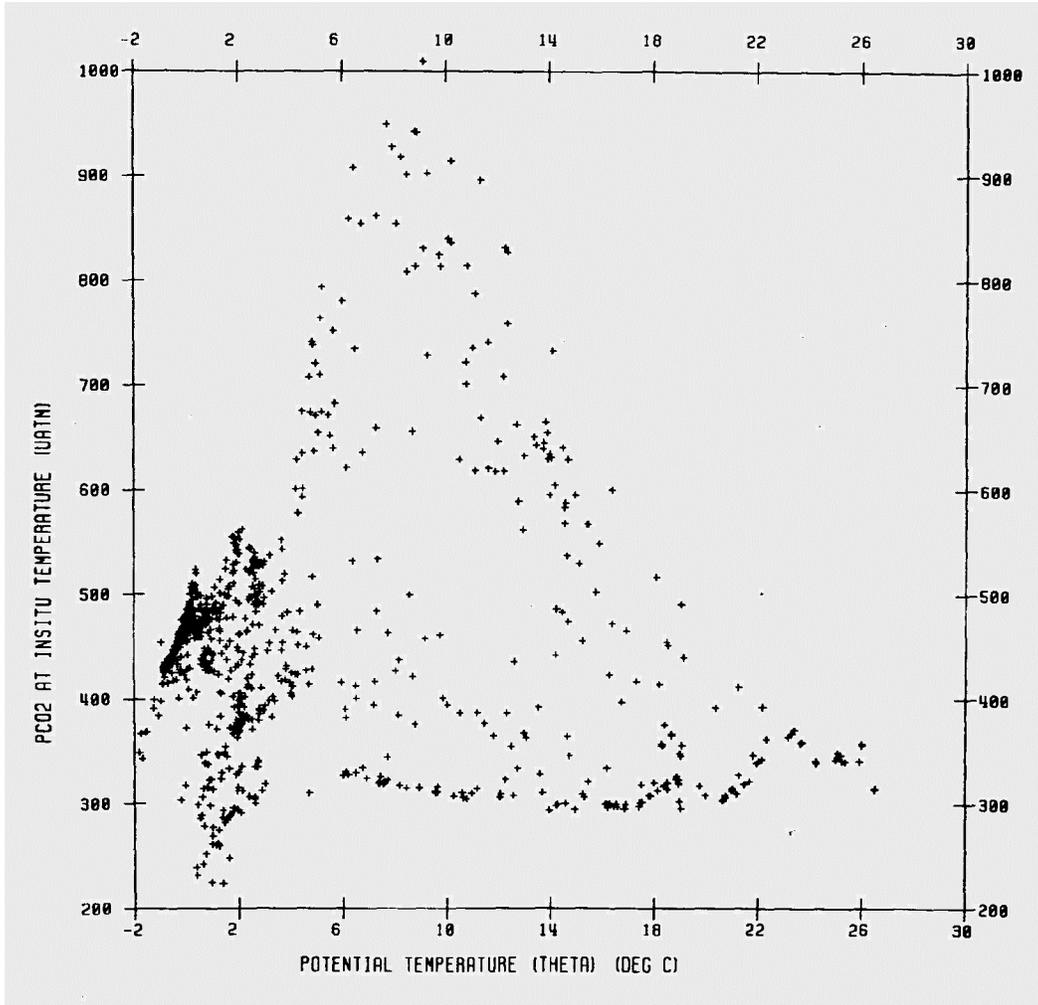
**Figure 14:** *pCO₂ (at in situ temperature) versus potential temperature*
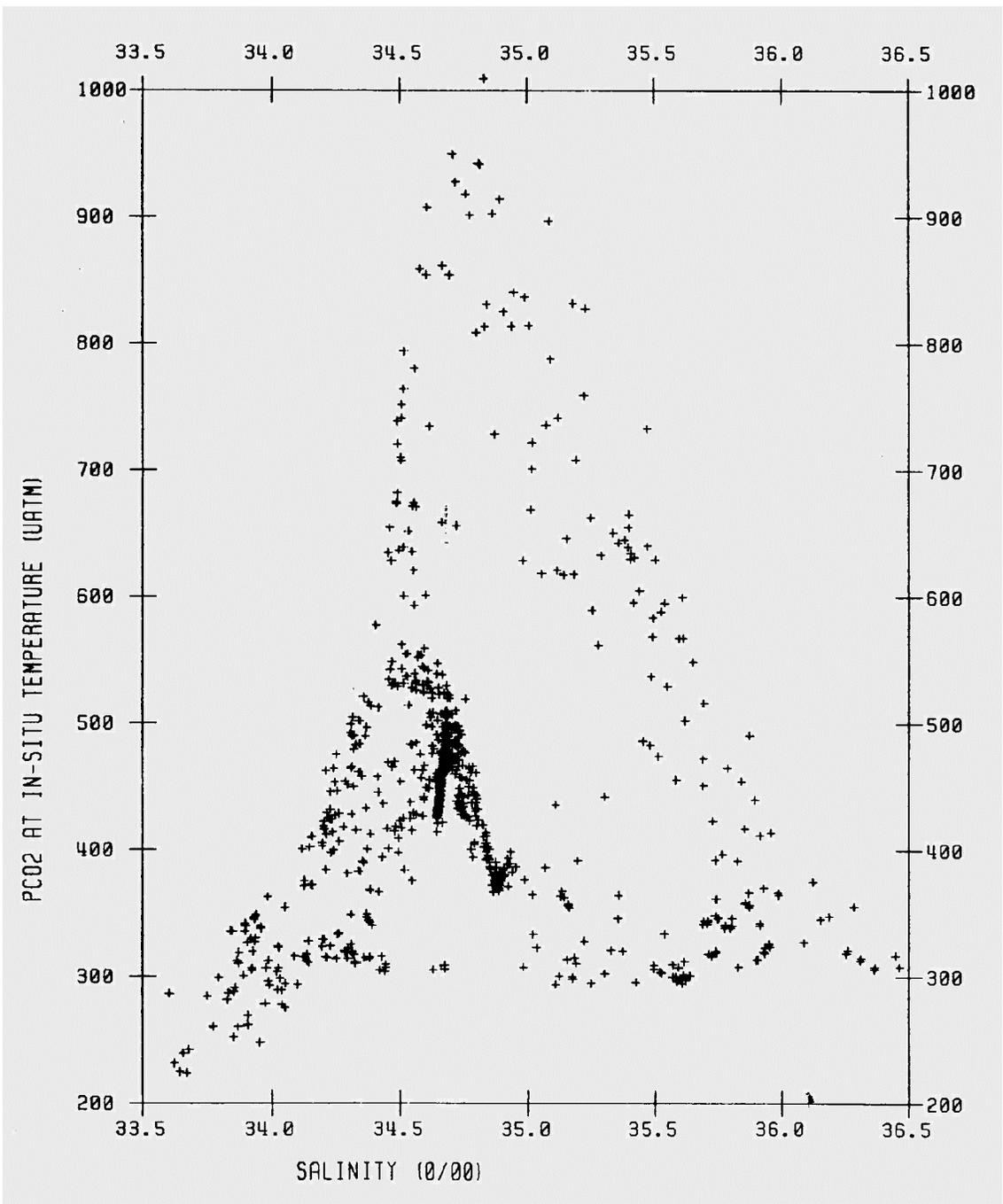
***Figure 15:*** *pCO₂ (at in situ temperature) versus salinity*
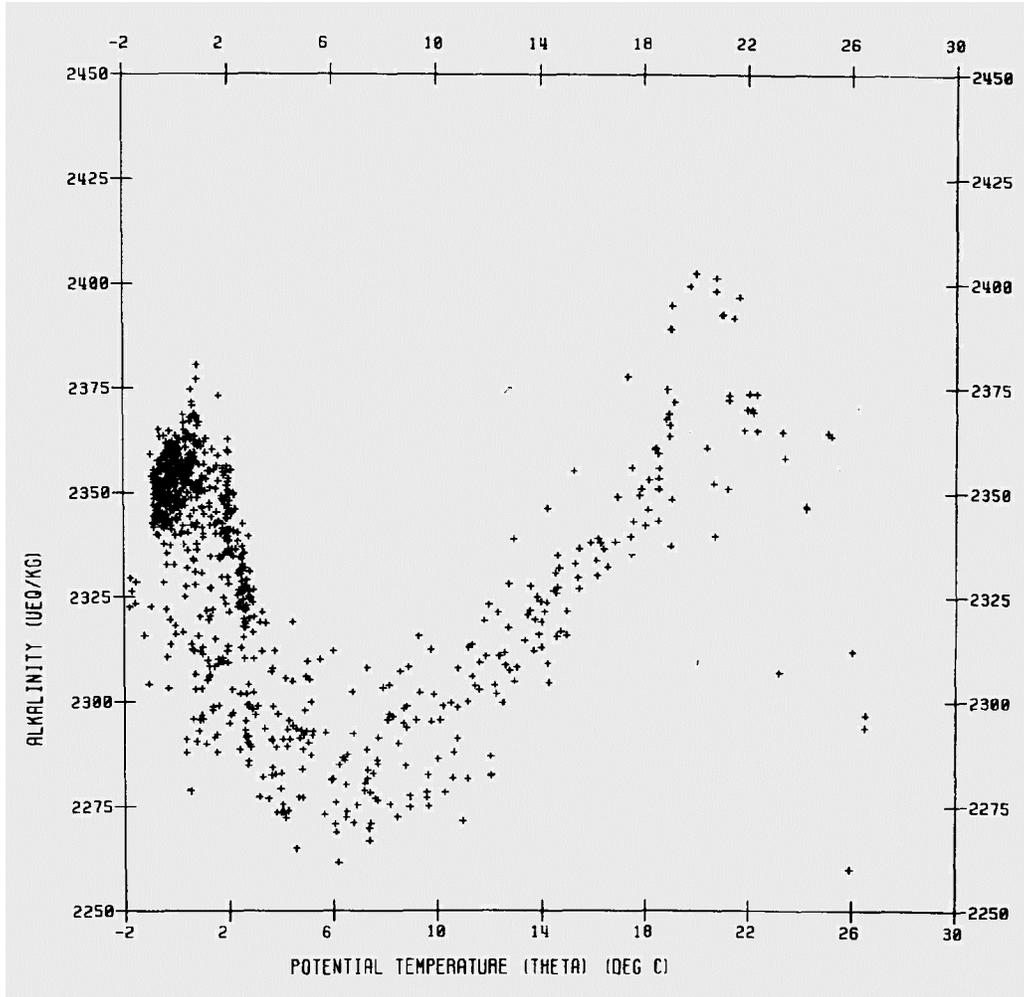
**Figure 16:** *Total alkalinity versus potential temperature*
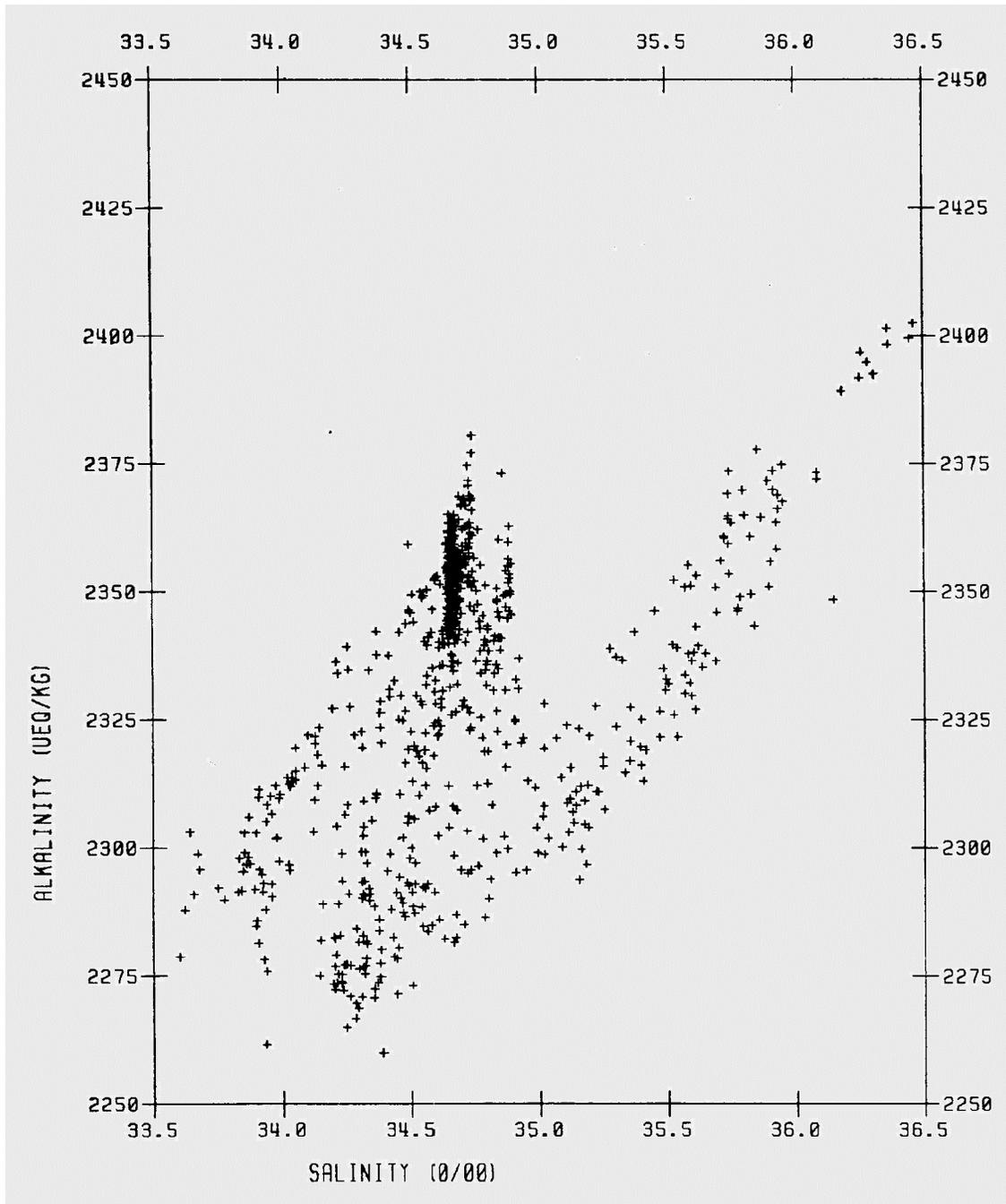
Figure 17: *Total alkalinity versus salinity*
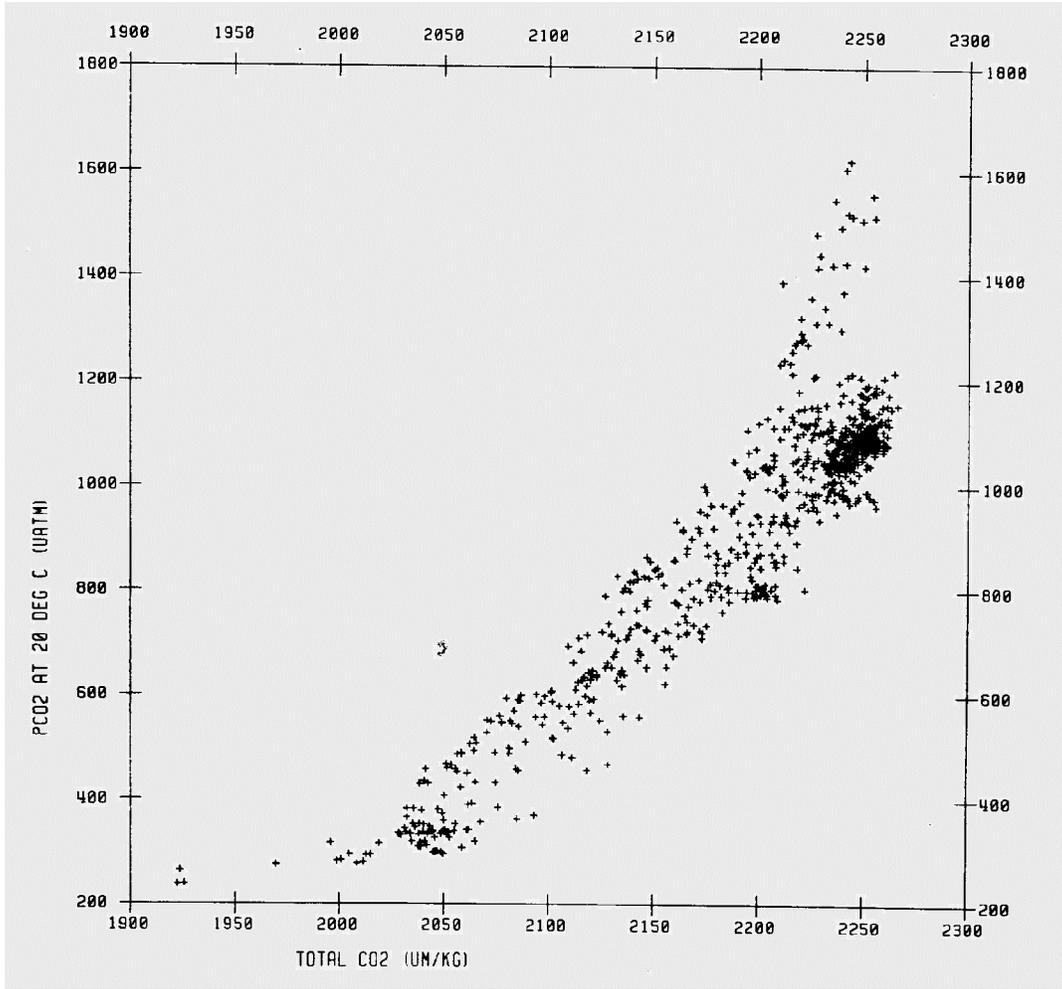
**Figure 18:** *pCO₂ (at 20°C) versus total CO₂ concentration*
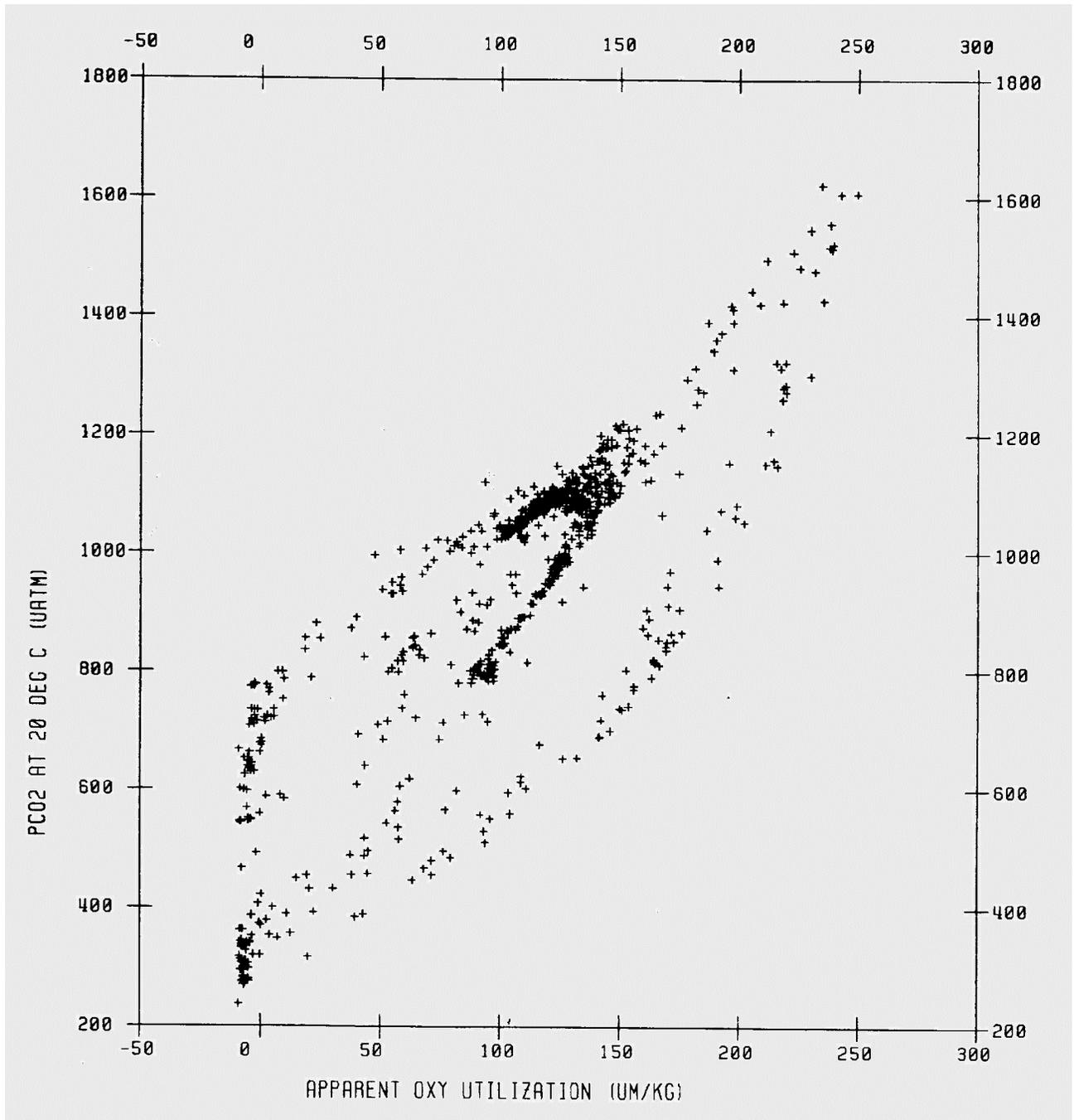
**Figure 19:** *pCO₂ (at 20°C) versus apparent oxygen utilization*
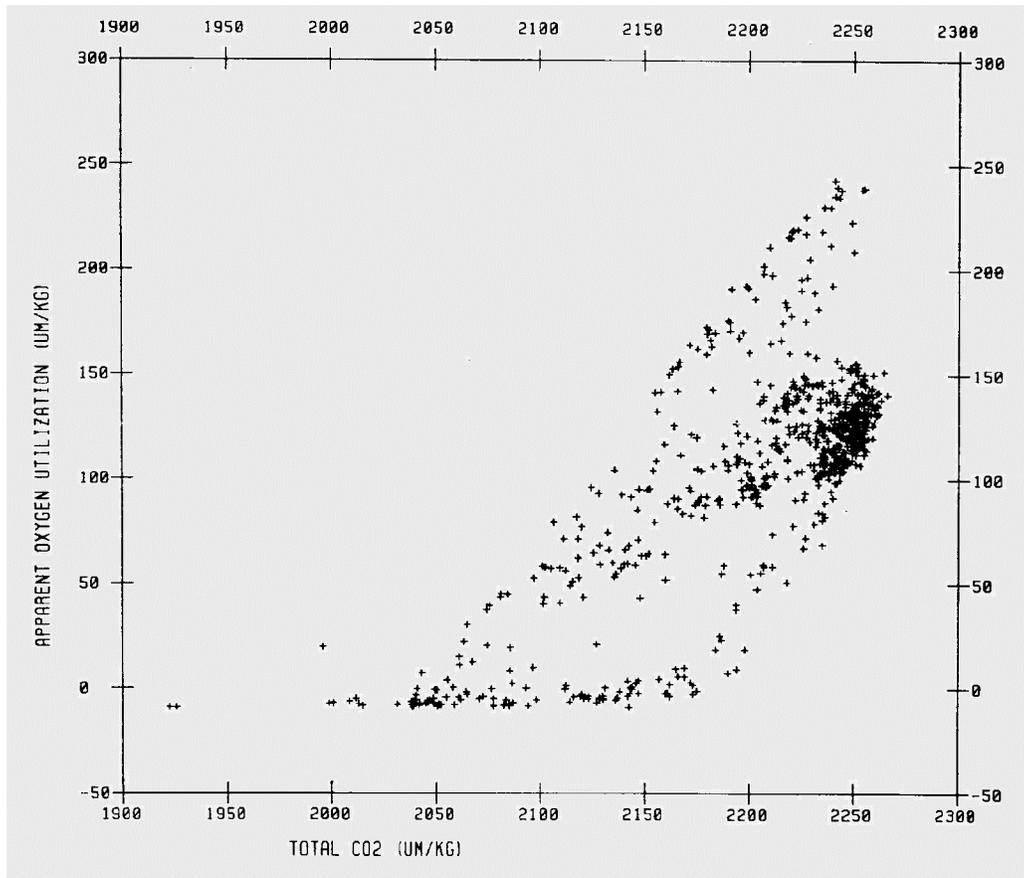
Figure 20: *Apparent oxygen utilization versus total CO$_2$ concentration*
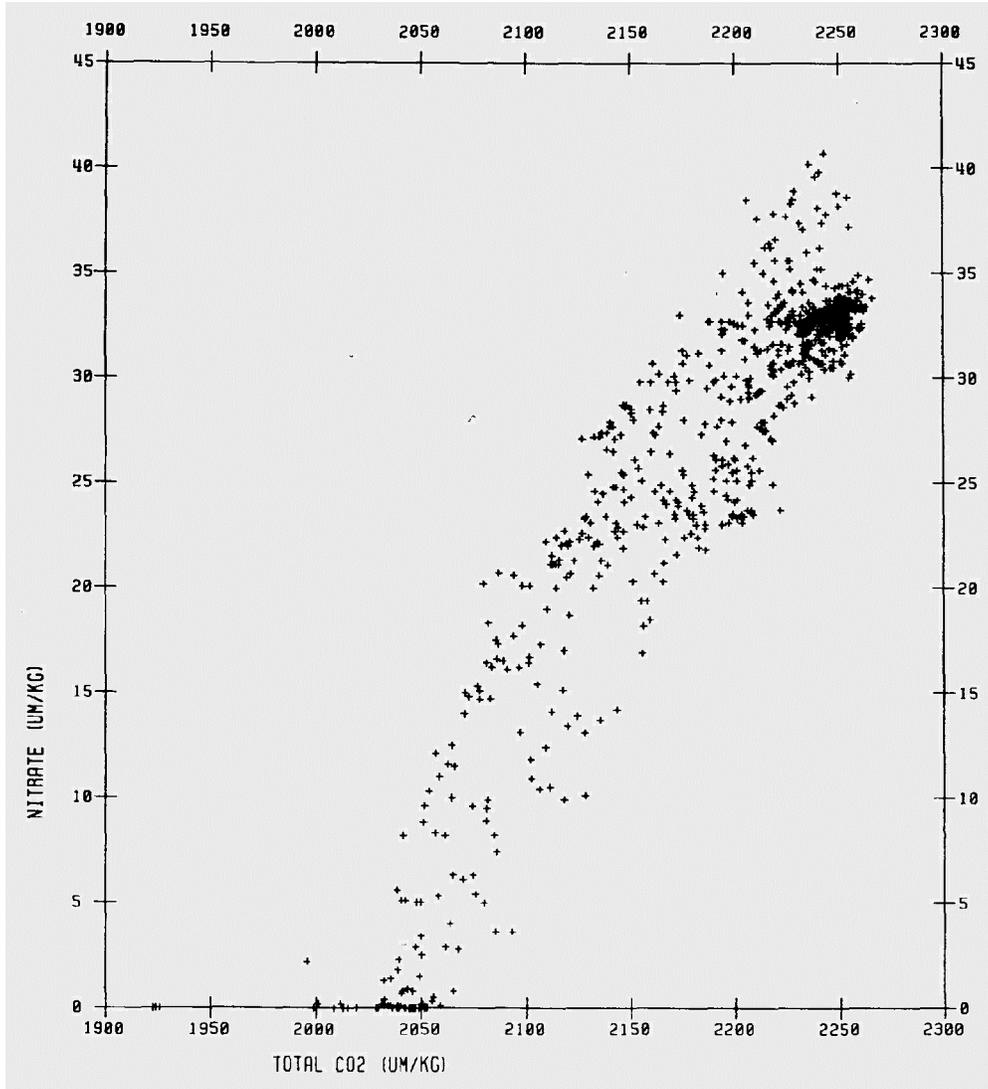
Figure 21: *Nitrate concentration versus total CO₂ concentration*
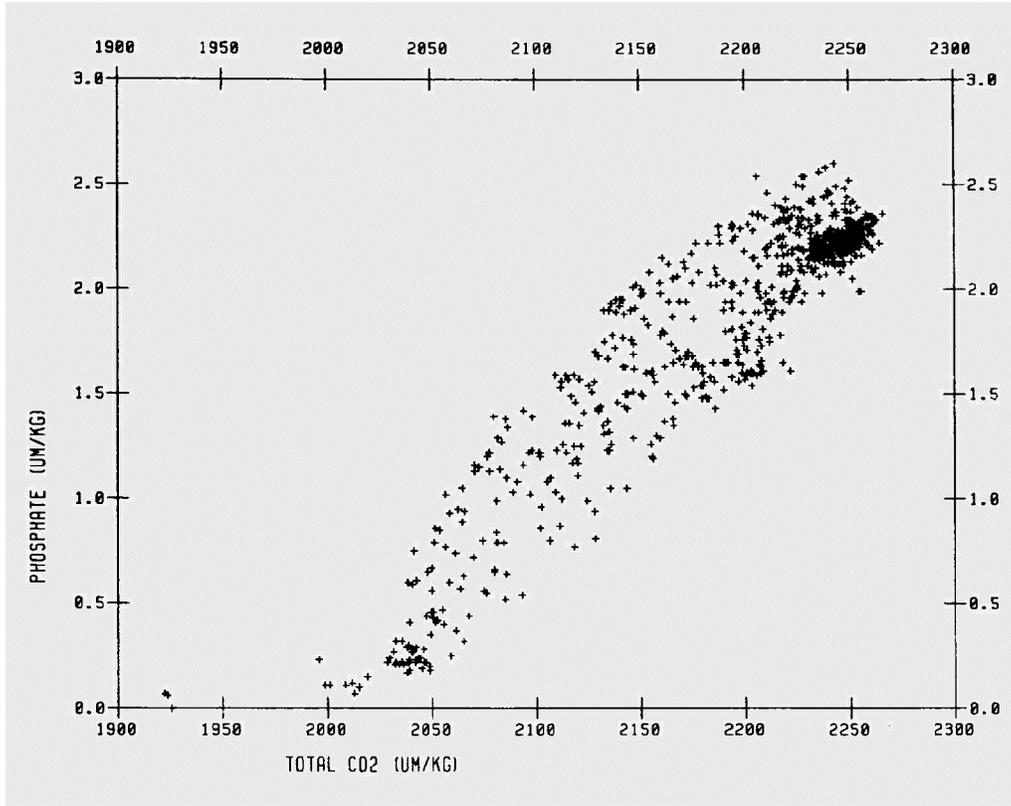
**Figure 22:** *Phosphate concentration versus total CO₂ concentration*
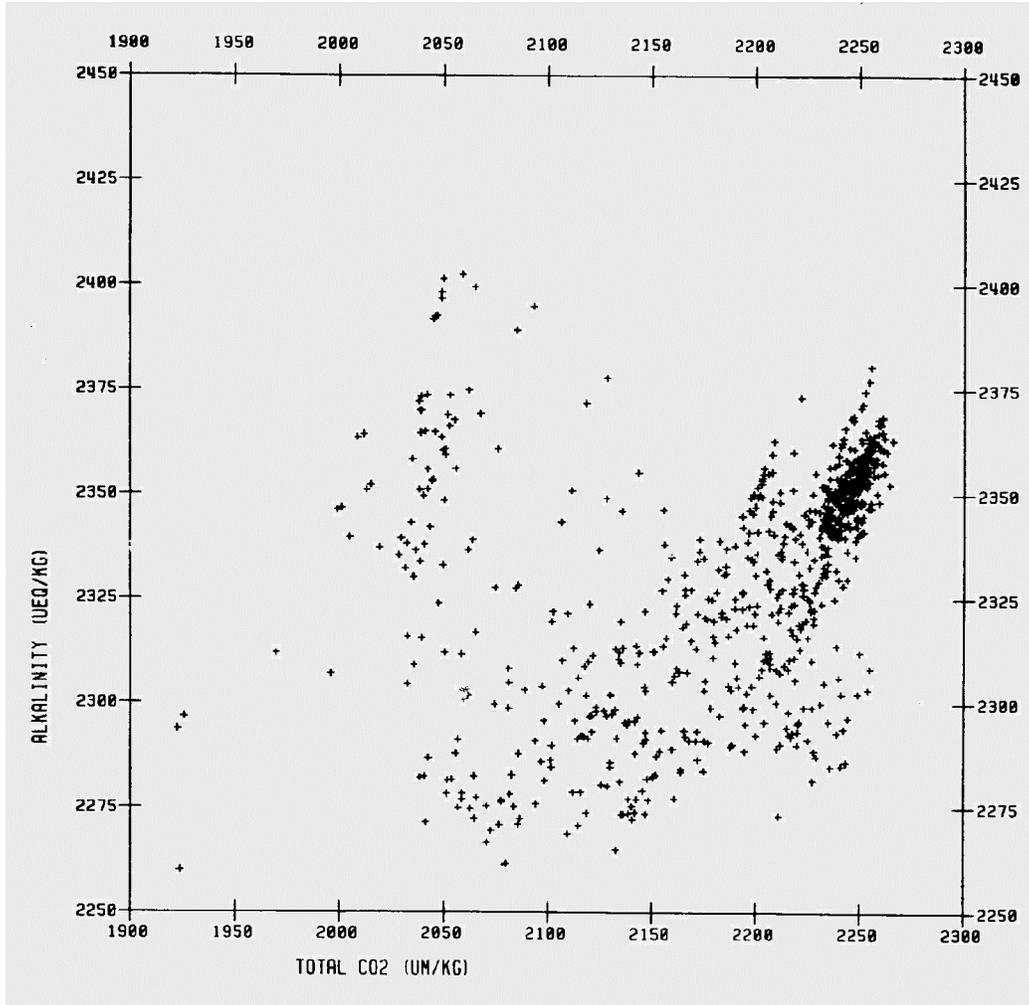
Figure 23: *Total alkalinity versus total CO₂ concentration*
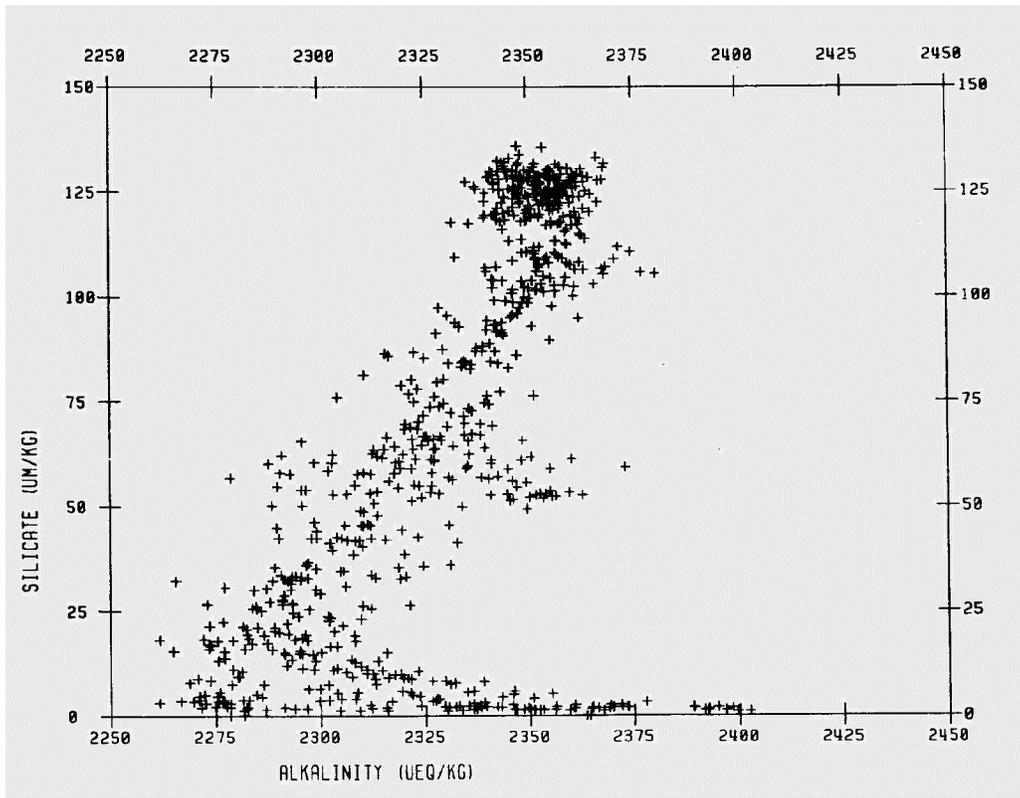
Figure 24: *Silica concentration versus total alkalinity*
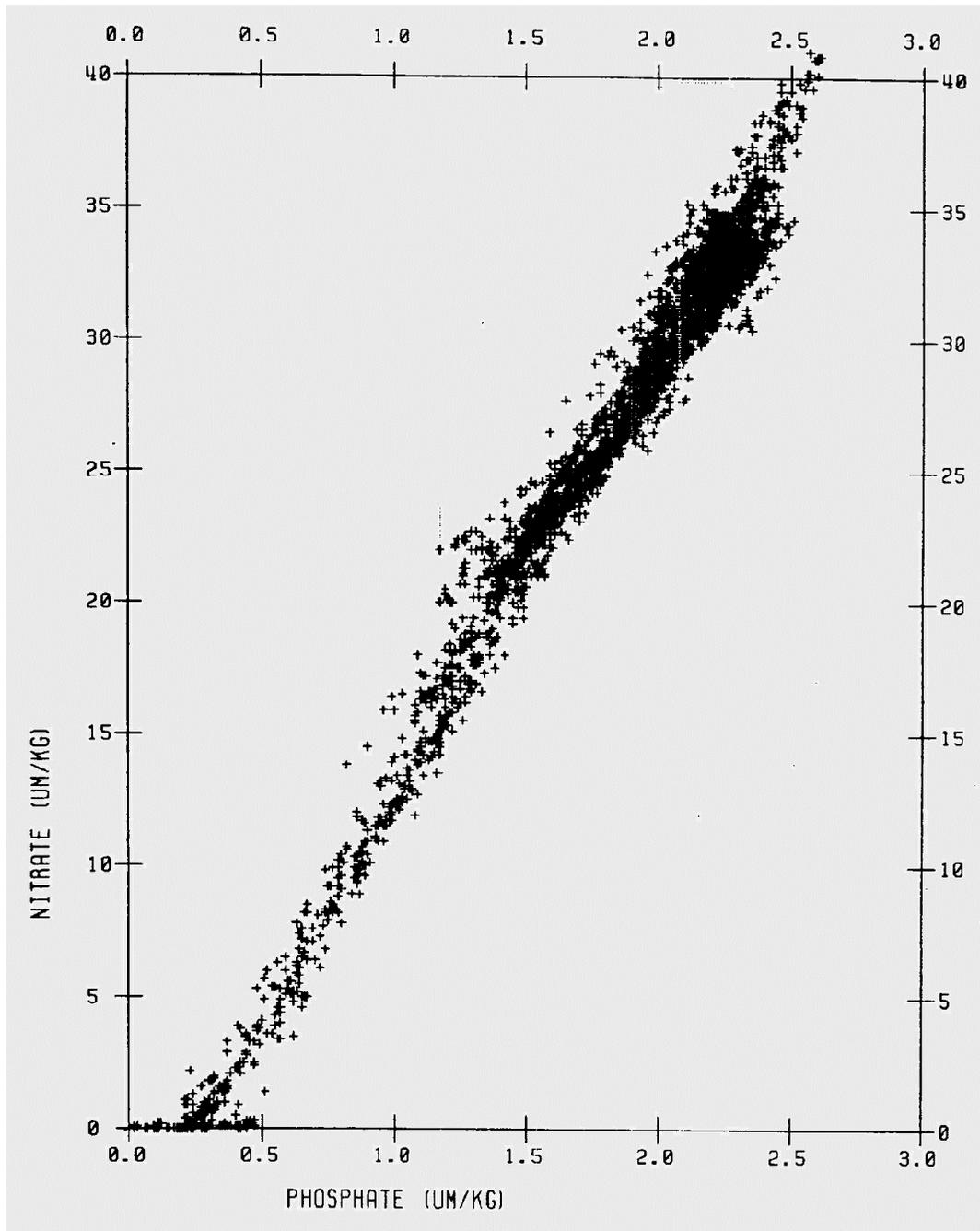
Figure 25: *Nitrate concentration versus phosphate concentration*
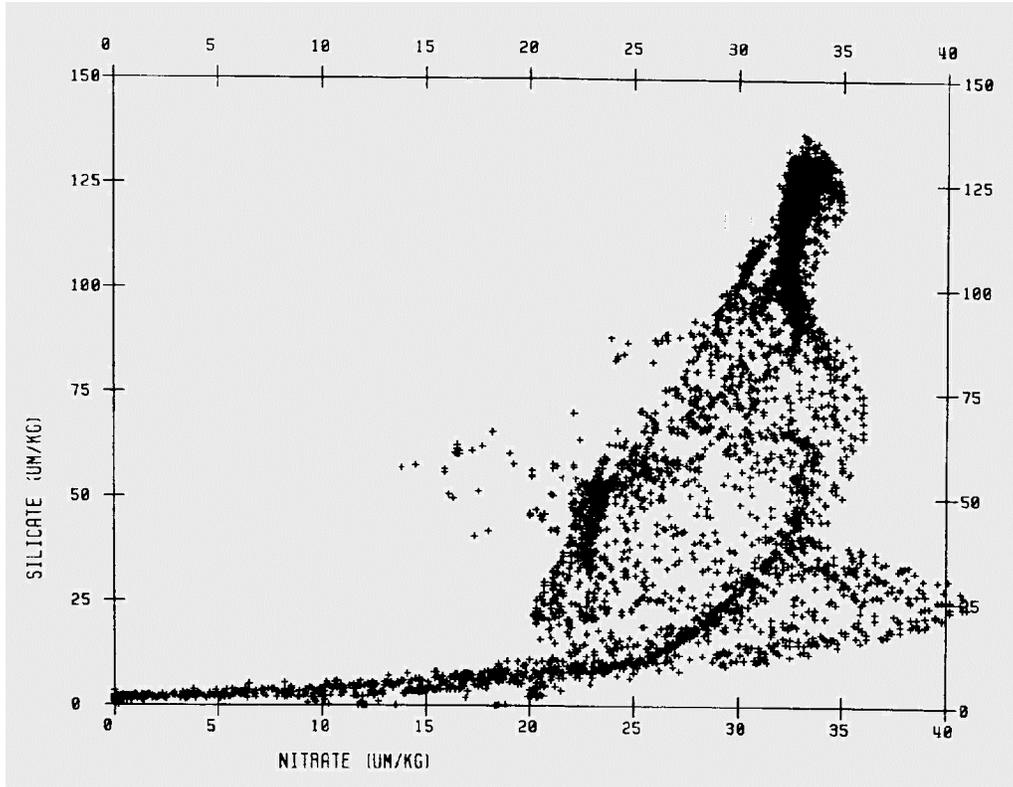
Figure 26: *Silica concentration versus nitrate concentration*

SECTION IV LONG–LINES (AJAX) SOUTH ATLANTIC AND SOUTHERN OCEAN CARBONATE CHEMISTRY DATA

With the exception of the carbonate chemistry parameters (pCO_2, TCO_2 and TALK), all of the data were obtained by the Physical and Chemical Oceanographic Data Facility (PACODF) of the Scripps Institution of Oceanography (see "Physical, Chemical and in–situ CTD Data from the AJAX Expedition in the South Atlantic Ocean", SIO Reference 85–24 and TAMU Reference 85–4–D, 275 pp., 1985).

The carbonate chemistry data obtained by the Lamont–Doherty Geological Observatory group consist of the partial pressure of CO_2 in seawater (pCO_2) (measured at a constant temperature of 20.00 °C) and the total dissolved carbon dioxide concentration in seawater (TCO_2). The TCO_2 data are represented in micromoles per kilogram (uM/kg). The partial pressure of CO_2 in seawater at 20.00 °C (rather than at in situ or potential temperature) is expressed in microatmospheres (uatm). The partial pressure of CO_2 at another temperature, T1, can be computed by using the following equation:

$$pCO_2(T1) = pCO_2(T20°C) \exp((T1-20) \times 0.043)$$

In addition to the observed quantities pCO_2 and TCO_2, the table includes the computed quantity TALK (total alkalinity), in microequivalents per kilogram (uEq/kg), and apparent oxygen utilization (AOU), in micromoles per kilogram (uM/kg). TALK is computed from the observed pCO_2 TCO_2 (GC determination only), salinity, silica (SiO_3) and phosphate (PO_4) concentrations, using the computer subroutine given in Appendix A. In a few cases TALK appears in the table in spite of the absence of pCO_2 and/or nutrient concentration values; in these cases a second Niskin sampler was tripped at the same depth and the values for the missing parameters are taken from the companion sampler. Data for the second sampler will normally be found on the immediately preceding or following line in the table. AOU has been computed by:

$$AOU = O_2(sat.,8) - O_2(obs.),$$

where $O_2(sat.,9)$ is the concentration of oxygen the water would have at its potential temperature if saturated with air, and $O_2(obs.)$ is the measured concentration of oxygen in the sample, both expressed in uM/kg. The value for $O_2(sat.,8)$ is computed using the solubility data of Weiss (1970).

The computed quantities "potential temperature", "sigma–theta", "sigma–2" and "sigma–4" have been calculated from the observed values of temperature, salinity and pressure using the UNESCO International Equation of State for Seawater (Millero et al., 1980), and the adiabatic temperature gradient expression of Fofonoff (1977), based on the results of Bryden (1973).

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Weiss, R.F., 1970, The solubility of nitrogen, oxygen and argon in water and seawater. *Deep-Sea Res.* **17**, 721-735.

APPENDIX A

```
C  **********  SUBROUTINE TALKX**********


C  TO CALCULATE TOTAL ALKALINITY (TALK) FROM TOTAL CO2 AND PCO2


C This is a FORTRAN 77 program using the symbol @ in column C six as a
continuation mark for a line of code longer than C 72 characters.


C  *******************************************************
C  * PROGRAMMER:  S. C. SUTHERLAND                       *
C  *              LAMONT-DOHERTY GEOLOGICAL OBSERVATORY   *
C  *              PALISADES, NY 10964                     *
C  *              U.S.A.                                  *
C  *              PHONE:  (914) 359 2900 EXTENSION 632    *
C  *******************************************************


      SUBROUTINE TALKX (ITEMP,I5ALIM,1PO4,15103,IPCO2,1TCO2,TALKO1J)
      REAL TEMP,SALIN.PO4,SI03,PCO2,TCO2,TALKOU,ITENP,ISALIN,1PO4
     1,131O3,1PCO2,ITCO2,K1CO2,K2CO2,K6,KCO2,K1PO4,K2PO4,KH2O
     2PKB,KSIO3,H2CO3,ASIO3,APO4,AH2O,ACO3,HCO3,CO3,ABORON.TBORON
     3,CB,CU,HION
      INTEGER I,J,K


C  The function "LOG" is the natural logarithm


C  UNITS:


C  TEMP IN DEG C.
C  SALINITY IN 0/00
C  PO4 IN UMOL/KG
C  SI03 IN UMOL/KG
C  PCO2 IN UATM
C  TCO2 IN UMOL/KG


C  VARIABLES WHICH BEGIN WITH I (IPCO2, ISI02. ETC.) ARE USED AS
C  INPUT VARIABLES, AND ARE MOVED TO WORKING VARIABLES WITHIN THE
C  SUBROUTINE, TO PROTECT THEIR SEPARATION FROM ANY CALLING ROUTINE


C  CONVERT UNITS TO MOLES/KG, ATMOSPHERES, AND DEG K.

      TEMP = ITEMP + 273.15
      SALIN = ISALIN
      PO4 = 1PO4 * 1E-6
      SI03 = 15103 * 1E-6
      PCO2 = IPCO2 * 1E-6
      TCO2 = ITCO2 * 1E-6


C  CALCULATE SOLUBILITY OF CO2 IN SEAWATER   KCO2

      KCO2 = EXP (-60.2409 + 9345.17 / TEMP  23.3585 *
     @  LOG (TEMP/100.) + SALIN * (0.023517 - 2.3656E-4
     *  TEMP + 4.7036E-7 * TEMP * TEMP))
```

```
C   Calculate solubility constants K1 & K2 of carbonic acid
C   as determined by Mehrbach, et. al. (Mehrbach, C., C.H. Culberson,
C   J.E. Hawley and R.M. Pytkowicz 1973,Limnology and Oceanography,
C   18, 897-907.)


C   K1CO2, K2CO2

      K1CO2 = 10. ** (13.7201 - 0.031334 * TEMP - 3235.76 / TEMP
     @ - 1.3E-5 * SALIN * TEMP + 0.1032 * SQRT(SALIN))


C   INTERMEDIATE VARIABLE K6

      K6 = ( -5371.9645 - 1.671221 * TEMP - 0.22913 * SALIN
     @ + 128375.28 / TEMP + 8.0944E-4 * SALIN * TEMP - 2.136
     @ * SALIN / TEMP * ( -18.3802 * LOG (SALIN) + 2194.3055
     @ * LOG (TEMP) + (5617.11 / TEMP) * LOG (SALIN)) / 2.302585)

      K2CO2 = EXP (2.302585 * K6)


C   Calculate dissociation constant of boric acid after Lyman (1956),
C   (Lyman, J. 1956, Buffer Mechanism of seawater,
C   ph.D. Thesis, Univ. of Calif., Los Angeles, 196 pp.)

      KB = 10. ** ( -9.26 + 0.00886 * SALIN + 0.01 * ITEMP)


C   Calculate dissociation constants for phosphoric acid after Kester
C   and Pytkowicz. 1967. (Kester. D.R. and R.N. Pytkowicz 1967,
C   Determination of the apparent dissociation constants of
C   phosphoric acid in seawater.
C   Limnology and Oceanograph, 12, 243-252)

      K1PO4 = EXP ( -9.039 -1450. / TEMP)

      K2PO4 = EXP ( 4.466 - 7276. / TEMP)


C   Calculate dissociation constant for silicic acid after Ingri (1959)
C   (Ingri, N., 1959, Equilibrium studies of polyanions IV. Silicate
C   ions in NaC1 medium, Acta Chemica Scandinavica, 13, 758-775.)

      KSI03 = 4.OE-1O


C   Calculate dissociation of water by the convention used by
C   Culberson and Pytkowicz (1973) (Culberson, C.H. and R.M. Pytkowicz,
C   1973, Ionization of water in seawater, Marine Chemistry,
C    1, 403-417.)

      KH2O = EXP (148.9082 - 13847.26 / TEMP - 23.6521 * LOG (TEMP)
     @ + ( -79.2447 + 3298.72 / TEMP + 12.0408 * LOG (TEMP))
     @ * SQRT(SALIN) - 1.9813E-2 * SALIN


C   Calculate activity of H+ ion by formulation of Takahashi, et.al.
C   (1982a) of Culberson and  Pytkowicz (1973) (Takahashi, T.,
```

```
C  R.T. Williams and D.L. Bos 1982a, Carbonate chemistry, in
C  "GEOSECS PACIFIC EXPEDITION", Vol. 3 Hydrographic Data,
C  1973-1974. W.S. Broecker, D.W. Spencer and H. Craig. U.S.
C  Government Printing Office, 78-82.)


   FH = 1.29 - 0.00204 * TEMP + 4.61E-4 * SALIN * SALIN
   @  - 1.48E-6 * SALIN * SALIN * TEMP

C  CALCULATE TOTAL BORON (BASED ON CULKIN, 1965)
C  (Culkin, F., 1965, The major constituents of sea water, in
C  CHEMICAL OCEANOGRAPHY, Vol. I, Chapter 4, First Edition,
C  J.P. Riley and G. Skirrow editors, Academic Press, London,
C  121-161.)

   TBORON = 4.106E-4 * SALIN / 35.

C  MAJOR CALCULATIONS BEGIN HERE:

   H2CO3 = KCO2 * PCO2

   HION = (K1CO2 + SQRT(K1CO2 * K1CO2 + 4. * K1CO2 * K2CO2
   @  * (TCO2 / H2CO3 - 1.))) / ( 2. * (TCO2 / H2CO3 * 1.))

   ACO2 = KCO2 * PCO2 * (K1CO2 / HION + 2. * K1CO2 * K2CO2
   @  / (HION * HION))

   ABORON = KB * TBORON  / (HION + KB)

   ASIO3 = KSIO3 * SIO3 / (HION + KSIO3)


   APO4 = PO4 * (1 / (1 + K1PO4 / HION + K1PO4 * K2PO4
   @  /  HION**2) + 2 / (1 + HION / K1PO4 + K2PO4 / HION)
   @  + 3 / ( 1 + HION / K2PO4 + HION * HION / (K1PO4 * K2PO4)

   AH2O = KH2O * FH / HION - HION / FH

   TALKOU = (ACO2 + ABORON + ASIO3 + APO4 + AH2O)/1.E-6

   HCO3 = K1CO2 * H2CO3 / HION

   CO3 = K2CO2 * HCO3 / HION

   RETURN
   END
```

Chlorofluorocarbon Measurements

R.F. Weiss, J.L. Bullister, M.J. Warner, F.A. Van Woy, P.K. Salameh
June, 1990

INTRODUCTION

This report contains the results of measurements of the chlorofluorocarbons (CFCs) F-11 (trichlorofluoromethane) and F-12 (dichlorodifluoromethane) dissolved in seawater and in the atmosphere as measured during Legs I and H of Ajax expedition aboard R/V *Knorr* of the Woods Hole Oceanographic Institution. Leg I extended from Abidjan, Ivory Coast, to Cape Town, South Africa, between 7 October and 6 November, 1983, and included Stations 1 - 59. F.A. Van Woy and M.J. Warner were the CFC analysts on this leg. Leg II extended from Cape Town to Punta Arenas, Chile, between ii January and 19 February, 1984, and included Stations 60 - 137. J.L. Bullister and F.A. Van Woy were the CFC analysts on this leg. Dissolved CFC concentrations were measured at most stations, with a total of 3276 analyses, and measurements of atmospheric CFC dry air mole fraction were made at regular intervals along the cruise track.

Hydrographic data were collected by the Oceanographic Data Facility of the Scripps Institution of Oceanography. This report includes hydrographic data for only those bottles from which CFC samples were analyzed. A complete listing of the hydrographic data is given in the expedition data report (Scripps Institution of Oceanography and Texas A & M University, 1985).

CFC MEASUREMENT TECHNIQUES

CFC measurements were carried out by shipboard electron-capture gas chromatography according to the methods described by Bullister and Weiss (1988). The results have been corrected for sampling and analysis blanks, the statistical variations of which can be responsible for occasional negative values near the detection limit. Sampling blanks generally decrease at the beginning of an expedition, as the equipment becomes cleaner with use. For Ajax expedition, the following median F-l1 and F-12 sampling blanks in picomoles per kilogram, as determined from analyses of deep waters at low latitudes which we believe to be CFC-free, were subtracted from all dissolved CFC measurements in the listed station intervals:

Stations	F-11	F-12
1 - 11	0.0228	0.0146
12 - 22	0.0074	0.0097
23 - 137	0.0034	0.0040

It is important to emphasize that the data have been edited to remove serious "flyers" and contaminated samples, and to correct gross numerical errors. However, not all of the data have yet been subjected to the level of scrutiny associated with careful interpretive work. Readers are therefore requested to contact the authors for any revisions in the data which may post-date this report, and to draw to our attention any suspected inconsistencies. The results are reported on the SIO 1986 calibration scale. The precision (± one s.d.) of the seawater measurements is about 1% or about 0.005 pmol/kg, whichever is greater, for

both CFCs. The precision of the atmospheric measurements is about 0.4% for both CFCs. The estimated systematic accuracy of the calibrations is about 1.3% for F-11 and 0.5% for F-12.

ATMOSPHERIC CFC DATA

Atmospheric CFC measurements were made at regular time intervals along the cruise track, using air pumped continuously from inlets located at the ship's bow or stern, depending upon the apparent wind direction. Measurements were made either on station or while the ship was underway. Typically a group of 3 to 4 measurements were made consecutively, with a single geographic position being recorded for each group. Atmospheric F- 11 and F-12 concentrations are reported as dry air mole fractions.

Atmospheric CFC concentrations at each hydrographic station location were determined by averaging measurements taken within ±7 days of a station and within a radius starting at 60 km, and increased in steps of 60 km, until a minimum of 5 air values were found. These mean values are reported in the station listings.

SEAWATER CFC DATA

Dissolved CFC concentrations are reported in picomoles per kilogram. CFC saturation percentages relative to the mean atmospheric CFC concentrations reported at each station, and assuming a water-saturated atmosphere at the potential temperature of the sample and a barometric pressure of 1 atmosphere, are calculated using the solubility functions of Warner and Weiss (1985). F-11/F-12 ratios are included in the station listings for all water samples in which the measured F-11 and F-12 concentrations are both greater than 0.01 picomoles per kilogram.

Replicate CFC seawater samples were analyzed at routine intervals. These generally consisted of two or more syringes drawn from the same Niskin bottle, although a single syringe sample may occasionally have been analyzed twice. The individual replicate analyses are listed in a separate table, and their mean values are reported in the main bottle data listings, annotated with an "R".

Potential temperature is calculated from the equations of Fofonoff (1977). Potential density is calculated from the International Equation of State of Seawater (UNESCO, 1981) using potential temperature in place of in situ temperature. Oxygen percentage saturation is calculated from the solubility function of Weiss (1970).

The following single-character footnotes appear in the data listings:

CFC Footnotes	Hydrography Footnotes
R = mean of replicate measurements	H = from thermometric data (value normally from CTD)
M = manual peak integration	D = from CTD (value normally from discrete measurements)
I = irregular digital integration	U = uncertain data

CFC PROFILE PLOTS

CFC profiles from 5 stations are plotted on each page along with a map showing the locations of the 5 stations along the cruise track. Each profile is plotted on two concentration scales, differing by a factor of ten, so that features of the high-CFC surface waters and the low-CFC deep waters can both be seen. AU profiles are plotted on the same depth scale. Note that the concentration scales for Stations 1 - 47 are

different than for Stations 48 - 137. A dashed vertical line indicates zero concentration for each scale. The bottom depth is indicated where it is known and is on scale. At stations where the reported bottom depth is shallower than the deepest reported bottle, the bottom has been drawn 10 meters below the deepest bottle.

CONTOUR SECTIONS

The F-11 contour sections were machine-generated using the optimal estimation method as adapted by Roemmich (1983). Contours are in units of picomoles per kilogram, and are spaced at approximately logarithmic intervals in which each successive contour above 0.05 pmol/kg represents a doubling in concentration. The bottom has been drawn using the bottom depths reported with the hydrographic data. At stations with missing bottom depths, values were interpolated from adjacent stations. At stations where the reported bottom depth is shallower than the deepest reported bottle, the bottom has been drawn 10 meters below the deepest bottle.

ACKNOWLEDGEMENTS

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Fofonoff, N.P. (1977) Computation of potential temperature of seawater for an arbitrary reference pressure. *Deep-Sea Research* **24**, 489-491.

Roemmich, D. (1983) Optimal estimation of hydrographic station data and derived fields. *Journal of Physical Oceanography* **13**, 1544-1549.

Scripps Institution of Oceanography, The University of California at San Diego and Department of Oceanography, Texas A&M University (1985) *Physical, Chemical and in-situ CTD Data from the Ajax Expedition in the South Atlantic Ocean.* 275 pp.

UNESCO (1981) Background papers and supporting data on the International Equation of State of Seawater 1980. *UNESCO Technical Papers in Marine Science,* **38**, 192 pp.

Warner, M. J. and R. F. Weiss (1985) Solubilities of chlorofluorocarbons 11 and 12 in water and seawater. *Deep-Sea Research* **32**, 1485-1497.
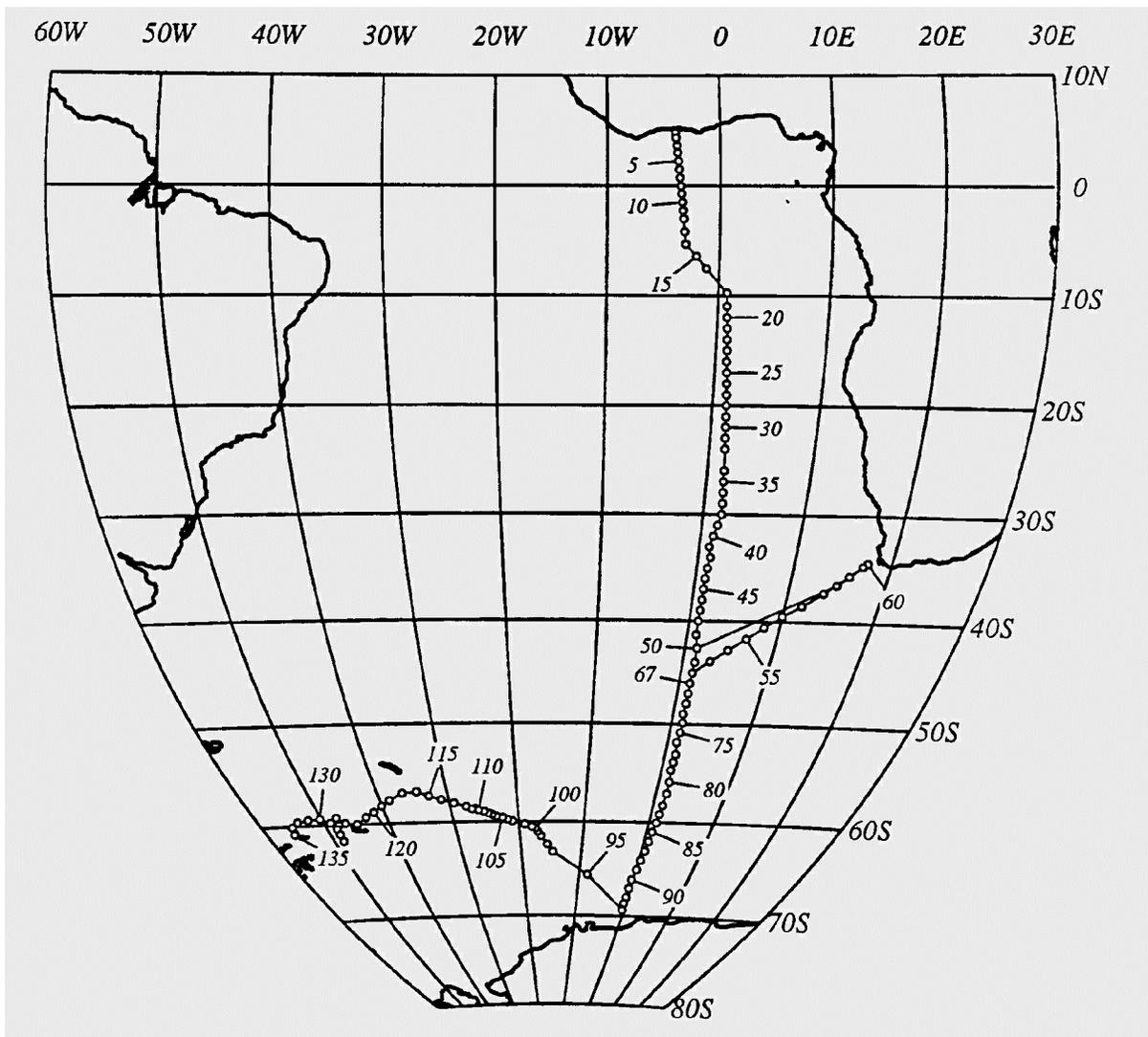
AJAX Station Locations where CFCs were Measured
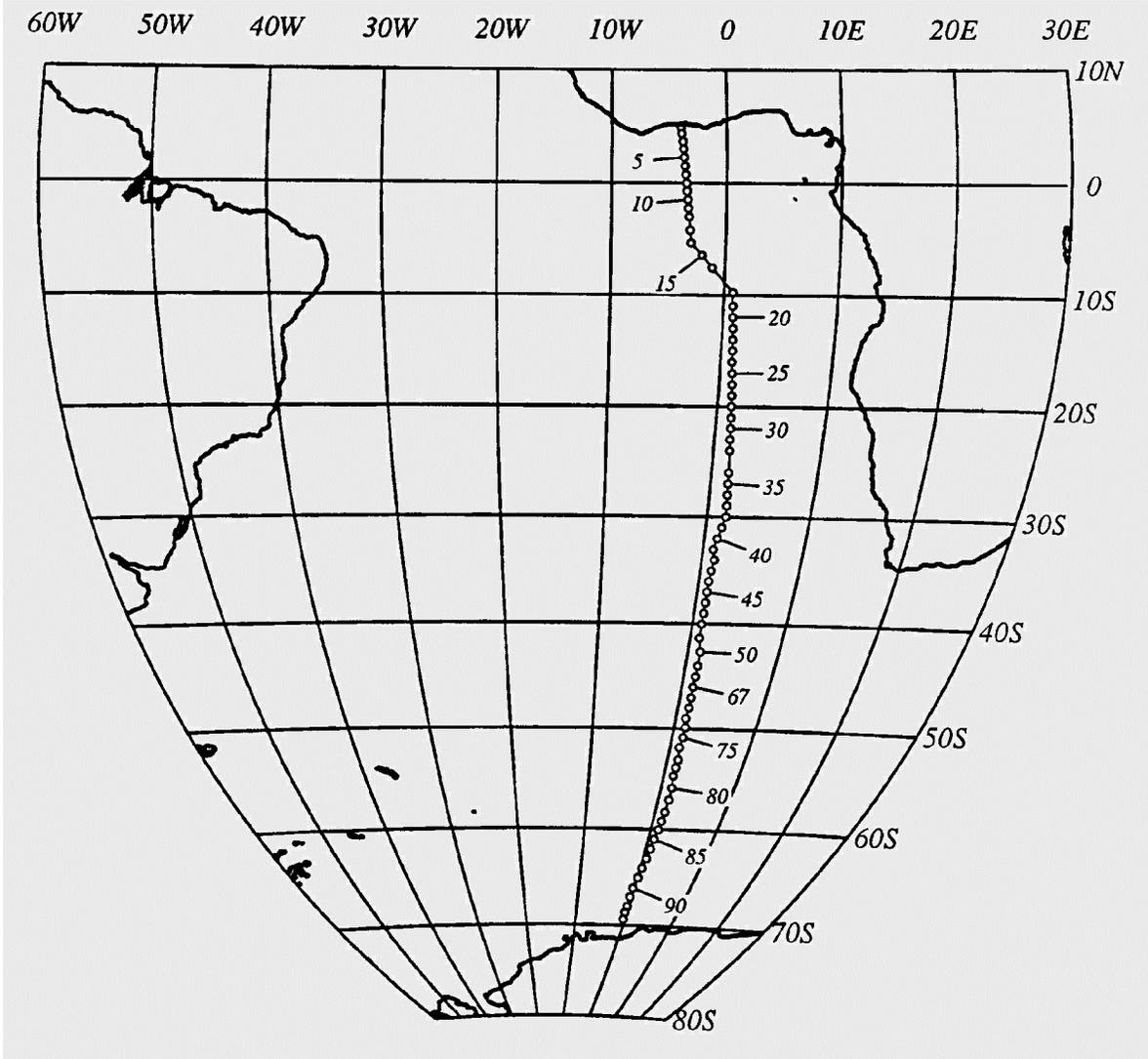
AJAX F-11 Section A Station Locations
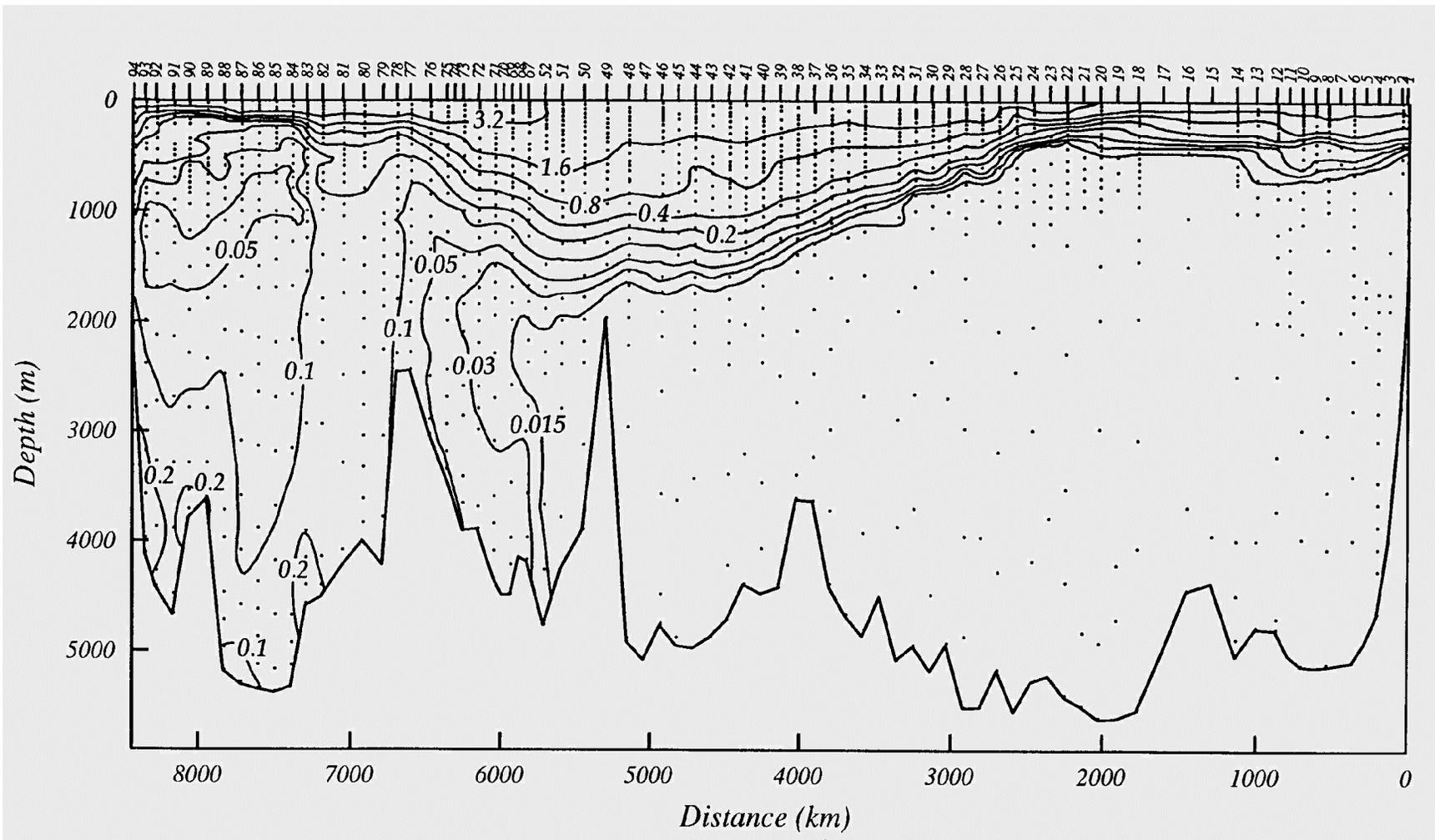
AJAX F-11 Section A: *F-11 concentrations in pMol/kg contoured as a function of depth and distance. Station numbers are indicated along the upper axis. Antarctica is on the left and Africa is on the right.*
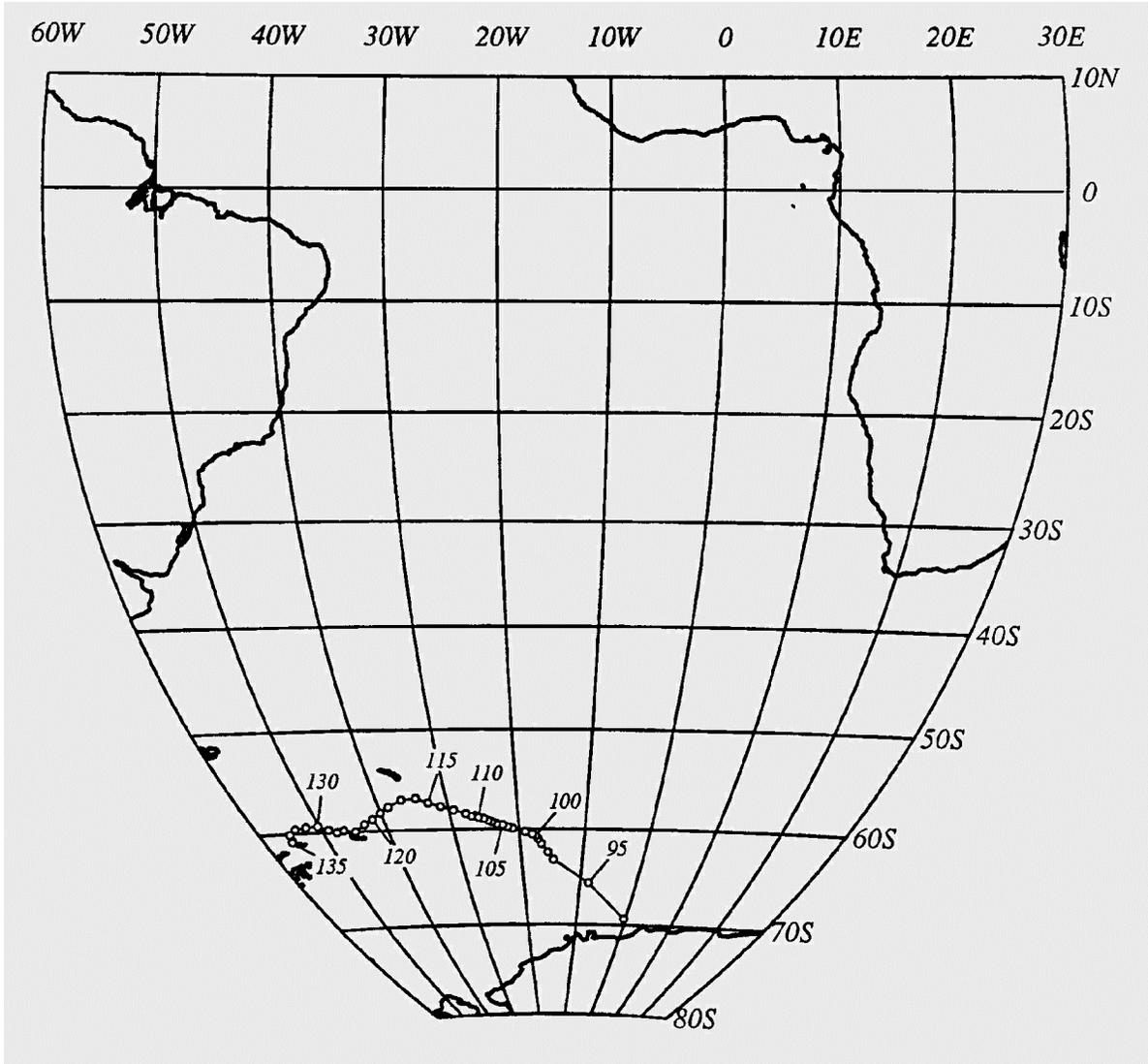
Ajax F-11 Section B Station Locations
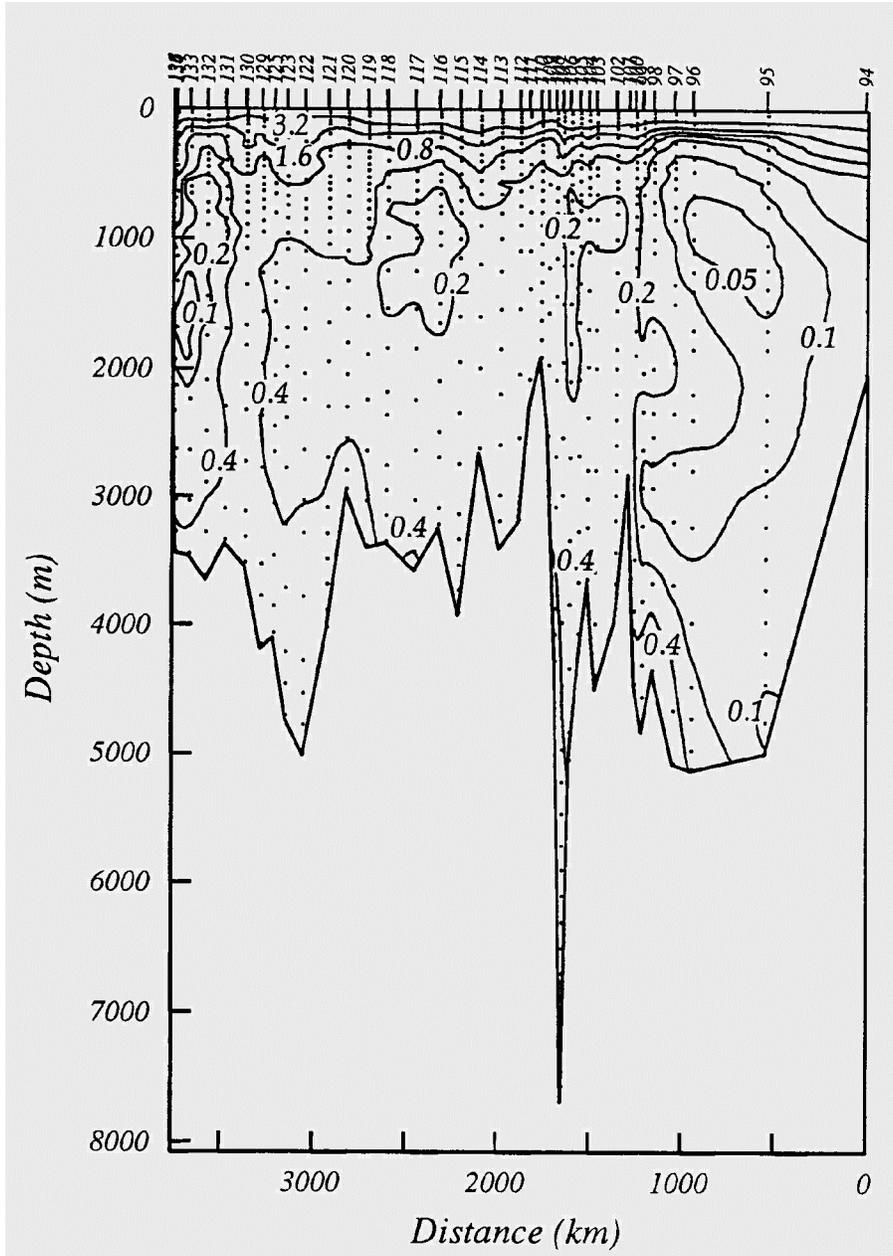
AJAX F-11 Section B: *F- 11 concentrations in pMol/kg contoured as a function of depth and distance. Station numbers are indicated along the upper axis.*

Data Processing Notes

Event Date	Contact	Data Type	Summary
2010-04-30	Bartolocci, Danie	BTL	Downloaded from CDIAC
	Grabbed the file below and crunched it through over here. One thing- PCO2 has units of PPM (my brain reads part per million) and not UATM, but I'm not a chemist. Are those units correct?		
	Oh yeah, you and Alex both treat the AJAX expedition as one cruise (Knorr 11/5), but we have it under two separate expos. I've just asked Jim if we should be splitting, but was there a reason you kept it as one file/cruise? Leg 1 ended in Nov and leg 2 doesn't start till Jan.		
	On Apr 29, 2010, at 2:38 PM, Robert Key wrote: > My version of the bottle data is posted at CDIAC > bob		
2010-05-04	Diggs, Steve	Cruise ID	Split data files into 2 cruises
	Just talked to Jim, and since there's a cruise in between the two AJAX legs, it's a definite "split". So please split-up the one file from CARINA into two files/cruises.		
2010-05-06	Bartolocci, Danie	BTL	Data online

2010.05.05 DBK

- As per Bob Key's email of 2010.04.30, PPM was changed to UATM.
- Jim Swift confirmed split of original bottle file into two legs.
- Generated netCDF files and checked in JOA. Zipped files into ajax_316N19831007_nc_ hyd.zip.

The notes below apply to all formatting and splitting of the original ajax_316N19831007 bottle file.

Leg one has been placed online. Notes file sent to Jerry.

2010.04.30 DBK

Reformatting notes for the ajax_316N19831007 bottle file. This file was obtained from CDIAC, originally submitted to CDIAC by Bob Key. Original file named 316N19831007.exc.csv

This file contained both legs and was originally reformatted as one file. However, since the cruise was marked by over a month between legs, the files were split into two cruises.

leg 1: ajax_316N19831007
leg 2: ajax_316N19940111

This directory contains leg 1, which was subsequently split off of the originally formatted file containing both legs.

At this time, it is unclear which file scheme should go online, until resolved, the original file will remain (both legs).

Following edits were made to parameter and units headers:

- DBARS to DBAR
- DEGC to DEG C
- PCO2_TMP to PCO2TMP

*NOTE: PCO2 currently has units of PPM. CCHDO accepted units are UATM. Units will stand at this time but will be brought to Bob's and Alex's attention for clarification.

New parameter RA-8/6 and RA-8/6E were added to the parameter list in order to format check and re-order the file. This parameter is RA 228/226 Ratio and error, W. Moore is PI.

File was re-ordered using copy_bottle_data.rb

Name/date stamp was added.

Edited file named ajax_316N19831007_hy1.csv

File was visually checked with JOA. No netCDF files were generated at this time. WOCE formatted file was generated using exchange_to_wocebot.rb. File was visual inspected for format errors and placed online. WOCE file named ajax_316N19831007hy.txt