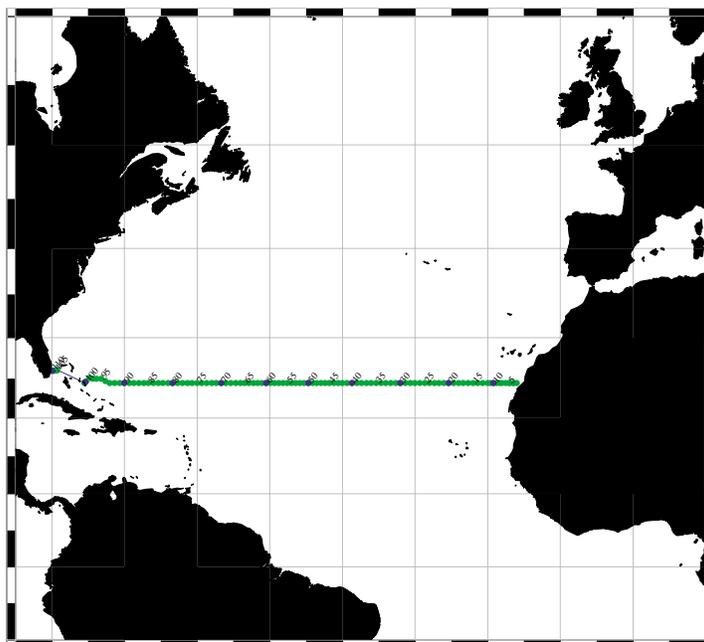


## A. Cruise Narrative: A05

(Updated June, 2007)



### A.1. Highlights

#### WHP Cruise Summary Information

WOCE section designation	<b>A05</b>			
Expedition designation (EXPOCODE)	<b>29HE06_1-3</b>			
Chief Scientists and their affiliation	<b>Gregorio Parrilla / IEO*, Harry Bryden / SOC**</b>			
Ship	<i>B.I.O. Hespérides</i>			
Dates	Leg 1: July 14 to July 17, 1992 Leg 2: July 17 to July 18, 1992 Leg 3: July 19 to August 15, 1992			
Ports of call	Leg 1: Cádiz to Sta. Cruz de Tenerife. Leg 2: Sta. Cruz de Tfe. to Las Palmas de G.C. Leg 3: Las Palmas de G.C. to Miami			
Number of stations	118			
Station geographic boundaries	80°03.95'W	26°04.19'N	15°58.08'W	
		24°28.40'N		
Floats and drifters deployed	none			
Moorings deployed or recovered	none			
Contributing Authors				
E. Álvarez	A. Cruzado	J. Escánez	M. Garcia	M.J. Garcia
J. García-Braun	M.D. Gelado	J.J. Hernández	R. Millard	F. Millero
R. Molina	A.F. Ríos	G. Rosón	W. Smethie	Z.R. Velásquez

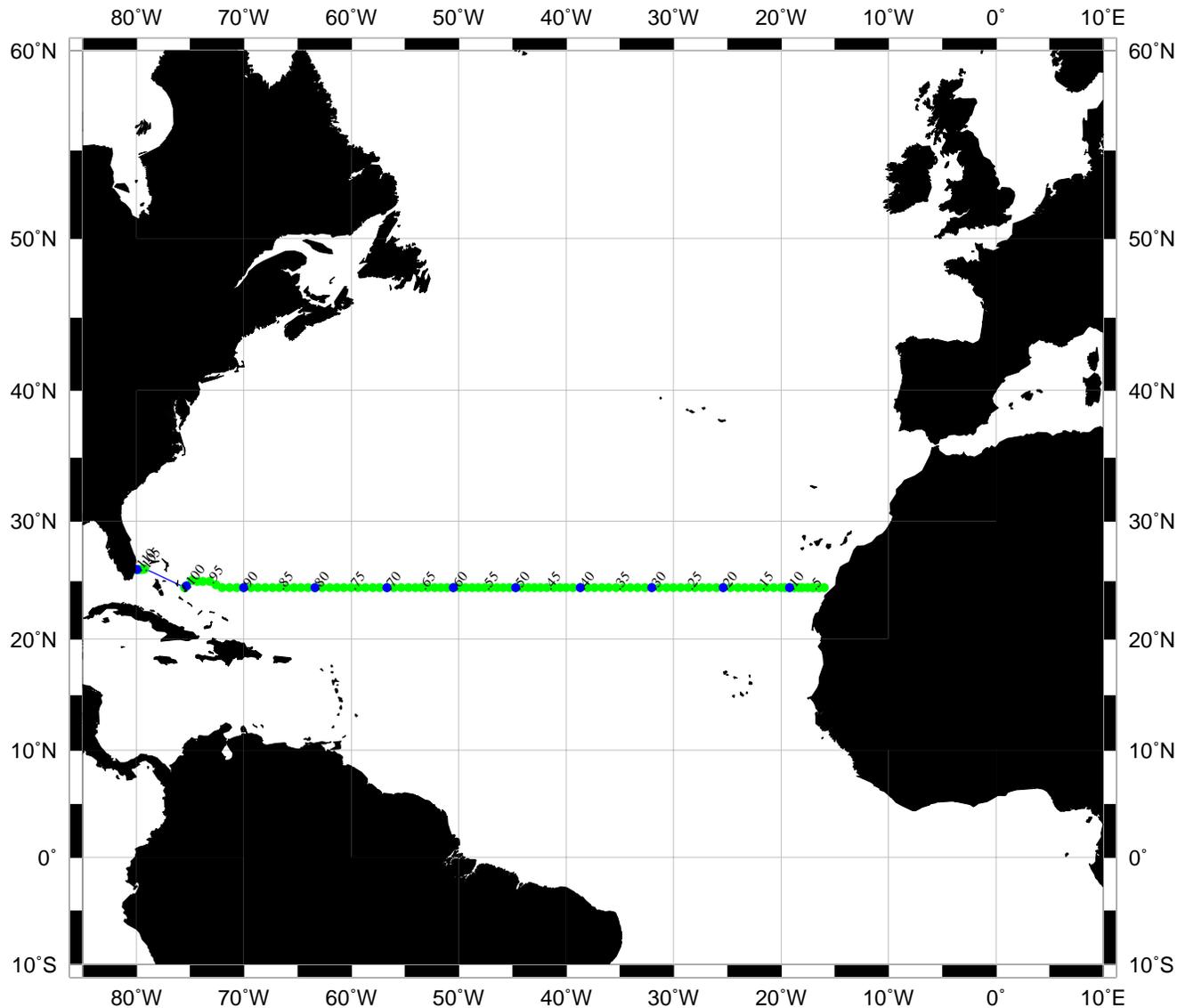
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Email: harry.bryden@soc.soton.ac.uk

Instructions: Click on headings below to locate primary reference or use navigation tools above. (Shaded headings were either not relevant to this cruise or not available when this report was assembled)

<b>Cruise Summary Information</b>	<b>Hydrographic Measurements</b>
<p>Description of scientific program</p> <p>Geographic boundaries of the survey</p> <p>Cruise track (figure)</p> <p>Description of stations</p> <p>Description of parameters sampled</p> <p>Bottle depth distributions (figure)</p> <p>Floats and drifters deployed</p> <p>Moorings deployed or recovered</p> <p>Principal Investigators for all measurements</p> <p>Cruise Participants</p> <p>Problems and goals not achieved</p> <p>Other incidents of note</p>	<p><b>CTD Data</b></p> <p>CTD - general</p> <p>CTD - pressure</p> <p>CTD - temperature</p> <p>CTD - conductivity/salinity</p> <p>CTD - dissolved oxygen</p> <p><b>Bottle Data</b></p> <p>Salinity</p> <p>Oxygen</p> <p>Nutrients</p> <p>CFCs</p> <p>Helium</p> <p>Tritium</p> <p>Radiocarbon</p> <p>CO2 system parameters</p> <p>Other parameters</p>
<b>Underway Data Information</b>	<b>DQE Reports</b>
<p>Navigation</p> <p>Bathymetry</p> <p>Acoustic Doppler Current Profiler (ADCP)</p> <p>Thermosalinograph and related measurements</p> <p>XBT and/or XCTD</p> <p>Meteorological observations</p> <p>Atmospheric chemistry data</p>	<p>CTD</p> <p>S/O2/nutrients</p> <p>CFCs</p> <p>14C</p>
<p><b>Acknowledgment</b></p> <p><b>CO2 Report</b></p> <p><b>Other BTL Data</b></p>	<p><b>References</b></p> <p><b>CO2 Report</b></p> <p><b>Other BTL Data</b></p>
<b>Data Processing Notes</b>	

# Station Positions for A05 • Parrilla & Bryden • 1992



*Produced from .sum file by WHPO-SIO*

### 1.1.2. Cruise summary

Cruise track is shown in [fig. 1](#). Situation and date of stations are given in [table I](#).

#### Sampling:

Water sampling included measurements of salinity both by CTD and bottle samples, CTD and bottle sample Oxygen determination, CTD temperature, nutrients (silicate, nitrate, nitrite and phosphate), CFC, pH, alkalinity, CO<sub>2</sub>, particulate matter, chlorophyll pigments, C14. Al. ADCP.

#### Type and Number of stations:

During the cruise 118 CTD/rosette stations were occupied using a 24 bottle rosette equipped with 10 or 12 liter in GO water sampling bottles; 6 test stations were made between Cadiz and Las Palmas de G.C., 101 on the A-5 section and 11 on the Strait of Florida Section. For navigation and placement of stations, GPS and dynamic positioning were used.

### 1.1.3. List of Principal Investigators

Name	Responsibility	Affiliation
G. Parilla	CTD	IEO
H. Bryden	CTD	JRC
R. Molina	S	IEO
J. Escáñez	O <sub>2</sub>	IEO
A. Cruzado	Nutrients	CEAB
W. Smethie	CFC	LDGO
A. Ríos	ph, Alk, CO <sub>2</sub>	IIM
F. Millero	ph, Alk, CO <sub>2</sub>	RSMAS
G. Rosón	Calcium	IIM
J. García Braun	Chlorophyll	IEO
Z. Velásquez	Chlorophyll	CEAB
J. Hernández	Al	FCMLP
W. Broecker	C14	LDEO
M. García	ADCP	UPC

### 1.1.4. Preliminary results

The ship departed from Cádiz on July 14, 1992 and 4 stations were made to test CTD and Rosette before arriving to Sta. Cruz de Tenerife on the 17th.

After the ship left Tenerife on the 18th and before arriving to L. Palmas the same day two more test stations were performed and the ADCP was checked.

During these stations several tests of a Falmouth Scientific Inst. CTD were also carried out.

The ship departed from L. Palmas in the early hours of the 20th to arrive to the first station of the section A-5 the same day. This section was finished, after 101 stations were made, at the Bahamas on August 14<sup>th</sup>. During the next day the Strait of Florida Section was completed and the cruise accomplished.

We carried 3CTDs, 2 belonging to IEO and 1 to WHOI. They are EG&G NBIS MARK III instruments equipped with Sensor Medics dissolved oxygen sensors and titanium pressure sensor (Millard et al 1991). All were calibrated at the WHOI facilities before the cruise. Because the delays inflicted by the hurricane Andrew on the equipment shipment from Miami to Woods Hole the post-cruise calibration were not performed on the CTDs until December. The conductivity and oxygen sensors were also calibrated at sea using the analysis of the water samples collected at each station. The depths of the sampling were based on the classical standard ones although they were varied on a station by station basis according to participants need to sample a particular layer provided there was no impairment of the in situ calibration activities.

Stn	Latitude	Longitude	Depth	Date	Time
1	24 29.97N	15 58.08W	51	07 20 92	17 23
2	24 29.96N	16 24.27W	120	07 20 92	20 07
3	24 29.95N	16 29.95W	570	07 20 92	21 31
4	24 30.18N	16 55.87W	1505	07 21 92	00 32
5	24 29.98N	17 04.93W	1895	07 21 92	05 47
6	24 29.72N	17 30.81W	2402	07 21 92	11 52
7	24 30.02N	18 00.04W	2555	07 21 92	16 02
8	24 29.43N	18 20.29W	2734	07 21 92	21 41
9	24 30.04N	18 45.04W	2944	07 22 92	02 22
10	24 30.08N	19 09.82W	3034	07 22 92	07 08
11	24 30.26N	19 35.04W	3378	07 22 92	22 25
12	24 30.20N	20 00.02W	3739	07 23 92	04 41
13	24 30.09N	20 40.01W	4162	07 23 92	11 12
14	24 30.00N	21 20.13W	4350	07 03 92	17 46
15	24 30.09N	21 59.07W	4673	07 04 92	01 00
16	24 29.85N	22 40.00W	4700	07 24 92	08 17
17	24 30.14N	23 20.32W	4991	07 04 92	15 22
18	24 30.04N	23 59.95W	5101	07 24 92	21 55
19	24 29.91N	24 40.21W	5197	07 05 92	04 23
20	24 29.90N	25 20.13W	5285	07 25 92	11 11
21	24 30.17N	25 59.92W	5347	07 25 92	17 40
22	24 30.17N	26 40.06W	4854	07 26 92	00 20
23	24 30.28N	27 19.65W	5536	07 26 92	06 51
24	24 30.00N	27 59.83W	5601	07 26 92	13 40
25	24 30.20N	28 39.39W	5655	07 26 92	20 15
26	24 30.16N	29 20.01W	5648	07 27 92	03 20
27	24 30.01N	29 59.90W	5408	07 27 92	09 57
28	24 30.01N	30 38.90W	5678	07 27 92	16 03
29	24 30.06N	31 20.27W	6080	07 27 92	22 45
30	24 30.17N	31 59.72W	5830	07 28 92	05 10
31	24 30.19N	32 39.57W	6320	07 28 92	12 05
32	24 29.95N	33 20.06W	6195	07 28 92	18 25
33	24 30.22N	33 59.85W	5650	07 29 92	01 24
34	24 30.27N	34 40.03W	5950	07 29 92	07 44
35	24 30.02N	35 19.85W	5035	07 29 92	14 22
36	24 30.10N	36 00.13W	5600	07 29 92	20 20
37	24 30.07N	36 39.91W	5020	07 30 92	02 55
38	24 30.06N	37 19.98W	5835	07 30 92	08 44
39	24 30.13N	38 00.05W	5567	07 30 92	15 38
40	24 30.14N	38 39.67W	4501	07 30 92	22 02
41	24 30.03N	39 19.93W	4370	07 31 92	03 39
42	24 30.15N	40 00.04W	5100	07 31 92	09 22
43	24 30.15N	40 34.85W	4572	07 31 92	14 45
44	24 29.95N	41 10.08W	5200	07 31 92	19 57
45	24 30.17N	41 44.97W	4789	08 01 92	01 37
46	24 30.00N	42 19.82W	4000	08 01 92	06 53
47	24 30.08N	42 54.88W	3574	08 01 92	12 15
48	24 30.02N	43 29.73W	3797	08 01 92	16 35
49	24 30.02N	44 04.85W	4177	08 01 92	21 39
50	24 30.21N	44 40.07W	3000	08 02 92	02 37
51	24 30.01N	45 15.08W	3640	08 02 92	07 00
52	24 29.93N	45 49.79W	2778	08 02 92	11 34
53	24 29.95N	46 24.91W	3511	08 02 92	14 58
54	24 29.95N	47 00.00W	3707	08 02 92	20 40
55	24 30.08N	47 34.98W	3980	08 03 92	01 25

Stn	Latitude	Longitude	Depth	Date	Time
56	24 29.84N	48 09.84W	3894	08 03 92	06 24
57	24 29.99N	48 44.97W	4379	08 03 92	11 27
58	24 30.03N	49 19.94W	5135	08 03 92	16 53
59	24 30.07N	49 54.77W	4796	08 03 92	22 29
60	24 29.90N	50 29.74W	4994	08 04 92	03 51
61	24 30.00N	51 04.95W	5076	08 04 92	09 25
62	24 30.08N	51 39.87W	4810	08 04 92	15 32
63	24 30.02N	52 14.99W	4728	08 04 92	22 03
64	24 29.99N	52 50.00W	5100	08 05 92	03 27
65	24 30.06N	53 24.93W	5637	08 05 92	09 04
66	24 29.92N	53 59.61W	6140	08 05 92	15 18
67	24 29.96N	54 40.00W	6209	08 05 92	21 34
68	24 29.94N	55 19.80W	5540	08 06 92	03 46
69	24 29.95N	56 00.01W	6444	08 06 92	09 57
70	24 30.03N	56 40.03W	6180	08 06 92	16 42
71	24 29.88N	57 19.79W	6116	08 06 92	23 51
72	24 29.91N	58 00.05W	6123	08 07 92	06 30
73	24 29.94N	58 39.96W	6071	08 07 92	13 09
74	24 30.08N	59 19.49W	5827	08 07 92	19 48
75	24 30.06N	60 00.12W	5937	08 08 92	02 04
76	24 30.00N	60 39.92W	5794	08 08 92	08 29
77	24 30.17N	61 19.40W		08 08 92	14 56
78	24 29.93N	61 59.88W	5891	08 08 92	21 37
79	24 30.07N	62 39.90W	5909	08 09 92	03 51
80	24 29.95N	63 20.12W	5850	08 09 92	10 33
81	24 29.95N	63 59.90W	5771	08 09 92	16 43
82	24 29.93N	64 39.94W	5762	08 09 92	23 12
83	24 30.37N	65 20.39W	5642	08 10 92	10 25
84	24 29.96N	65 59.98W	5764	08 10 92	17 05
85	24 30.04N	66 39.93W	5647	08 10 92	22 58
86	24 29.98N	67 19.99W	5658	08 11 92	05 14
87	24 30.01N	68 00.04W	5739	08 11 92	11 34
88	24 29.95N	68 39.93W	5712	08 11 92	17 32
89	24 29.92N	69 19.93W	5620	08 11 92	23 27
90	24 29.97N	70 00.00W	5561	08 12 92	05 20
91	24 29.87N	70 40.00W	5541	08 12 92	11 10
92	24 29.88N	71 19.92W	5519	08 12 92	16 50
93	24 30.00N	71 59.97W	5510	08 12 92	22 35
94	24 45.05N	72 35.94W	5497	08 13 92	04 10
95	24 59.80N	73 10.00W	5344	08 13 92	09 56
96	24 59.97N	73 49.95W	5242	08 13 92	15 38
97	25 00.00N	74 20.04W	4948	08 13 92	20 23
98	25 06.11N	74 49.77W	4702	08 14 92	01 47
99	24 32.77N	75 27.70W	3347	08 14 92	08 22
100	24 37.41N	75 19.12W	4800	08 14 92	11 45
101	24 30.00N	75 31.00W	930	08 14 92	16 03

Water samples were collected from 10 or 12 liters PVC Niskin GO bottles mounted on a GO Rosette Sampler. All the water sample conductivity and oxygen measurements were made in a constant temperature laboratory soon after each cast was completed. Descriptions of analytical techniques, precision and accuracy are given later in this report. Additional samples were also collected for the analysis of the other parameters listed above, description of which are presented in other sections of this report.

According to the WOCE Implementation Plan this line was located at 24°N. As two oceanographic sections had been made previously in 1957 and 1981) around 24.5°N (Roemmich and Wunsch, 1985) we asked the WOCEIPO to move the WOCE section A5 to this latitude, which was agreed to. With respect to the station separations and because we were constrained by ship time, we decided to use the following judgment: the first 6 stations were located at the 50, 100, 150, 1500, 2000 and 2500 isobaths (about 18nm separation). From there to the 4000m depth (stl2) the separation was about 23nm. From station 12 to the eastern limits of the Mid Atlantic Ridge we separated the stations by 36nm. Across the Ridge the separation was 32nm. From its western limits to the 5000 isobath near the Bahamas, stations were separated again 36nm. Stations close to the Bahamas were separated by less than 30nm. The stations across the Straits of Florida were occupied every 5nm.

Near to Bahamas we deviated the heading of the section slightly from the original plan in order to cross the continental slope perpendicular to the direction of the isobaths and to obtain a clear crossing of the Deep Western Boundary Current.

The ADCP and a thermosalinograph recorded continuous during the whole cruise. Wind information was recorded every hour.

At the end of the cruise the ship was checked for Tritium and C14 contamination by the Tritium laboratory of the University of Miami.

Vertical profiles for T, S and O<sub>2</sub> together with a listing of this data for standard depths for each station are given in the Annex.

#### **1.1.5. Incidents**

During the test stations, there were problems with the rosette: several of the bottles were not triggered. The trouble had to do, probably, with too much friction on the bolts since this rosette had never been used before. After some lubrication the problem disappeared. There were some problems, during the test stations and some of the first stations of the A-5 section, with the portside winch. The oil of the hydraulic circuit became too hot causing the winch to lose power. After station 11 we switched to the other winch that worked from the stern.

On station 62, CTD # 1 stop sending conductivity data and it was replaced by CTD # 2 until station 74 when CTD# 1 was brought back, only for 7 stations since we started getting pressure spiking. From station 81 to 88 we used CTD #2 and from there on we used CTD# 1 after it was repaired on board.

On station 83 the wire was reterminated after cutting off 10 m of wire because of a faulty electrical contact. It was also reterminated after station 110 (in the Florida Strait) because of two-blocking the CTD on recovery at this station.

On station 61 the CTD hit the bottom because of a failure of the depth recorder.

The portable hydrophone-recording system for use with the pinger failed from the beginning and we were not able to repair it. We tried to use the EA500 SIMRAD echo-sounder of the ship, but there was not the necessary documentation on board so we could not effectively use the pinger at all. We decided to keep the CTD package between 50 or 100 m above the bottom when the floor was too rough and less than 50 m when it was flat.

The proposed Tritium and Helium survey by Dr. Z. Top could not be made since the equipment was lost during shipment from Miami and it never arrived to the ship.

### 1.1.6. List of Participants

<b>Name</b>	<b>Responsibility</b>	<b>Affiliation</b>
G. Parrilla	Chief Scientist	IEO
H. Bryden	Co-Chief Scientist	WHOI
J. Alonso	CTD Watch	IEO
E. Alvarez	CTD Watch/Thermosalinograph	PCM
B. Amengual	S, O <sub>2</sub>	IEO
G. Bond	CTD Watch/CTD Electronics	WHOI
J. Garcia-Braun	O <sub>2</sub> , Chlorophyll	IEO
J. Hernández	AI	FCMLP
A. Cantos	CTD Watch/ADCP	Ainco I
A. Cruzado	Nutrients	CEAB
J. Escáñez	O <sub>2</sub>	IEO
S. Fiol	CO <sub>2</sub>	U. La Coruña
M.J. García	CTD Watch/Data Processing	IEO
D. Gelado	AI	FCMLP
E. Gorman	CFC	LDGO
A. Lavín	CTD Watch/Data Processing	IEO
R. Millard	CTD Watch/CTD Programming	WHOI
R. Molina	CTD Watch/S	IEO
J. Molinero	Electronics	IEO
A. Osiroff	CTD Watch/ Data Processing	SHMA
A.F. Ríos	CO <sub>2</sub> /M.O.P.	IIM
G. Rosón	Calcium	IIM
P. Sánchez	CTD Watch/Data Processing	IEO
W. Smethie	CFC	LDGO
Z. Velasquez	Chlorophyll	CEAB
A. Fougere	Falmouth SI CTD	WHOI
C. Heuer	Tritium/Helium	RSMAS
G. Mathieu	CFC	LDGO

### 1.1.7. Acronyms

IEO	Instituto Espanol de Oceanografia
IIM	Instituto de Investigaciones Marinas
CEAB	Centro de Estudios Avanzados Blanes
FCMLP	Facultad de C. del Mar
PCM	Programa Clima Maritimo
RSMAS	Rosenstiel School of Marine and Atmospheric Sciences
WHOI	Woods Hole Oceanographic Institution
LDGO	Lamont Doherty Geological Observatory
SHMA	Servicio de Hidrografia Naval
UPC	Unversidad Politecnica de Cataluna
JRC	James Rennell Centre

## **2. CTD MEASUREMENTS** (R. Millard and M.J. Garcia)

### **2.1. Instrumentation, Calibrations and Standards**

Two EG&G/NBIS Mark IIIb CTD underwater units each equipped with pressure, temperature, conductivity and plographic oxygen sensors were used throughout the cruise. The CTD instrument numbers are 1100 and 2326 and they belong to the Instituto Espanol de Oceanografia (IEO). Each CTD is configured identically with the same data scan length, variables, and scanning rate of 31.25 Hz. (A detailed description of the Mark IIIb CTD can be found in Brown and Morrison, 1978.) Both instruments were modified at Woods Hole Oceanographic Institution (WHOI) to add a titanium pressure sensor with a separately digitized resistive temperature device (RTD). A third EG&G/NBIS Mark IIIb CTD was provided by WHOI (WHOI instrument No. 8) but was not used during this expedition. A General Oceanics (GO) rosette fitted with 24 10 liters Niskin bottles was used with the CTD for collecting water samples. The GO rosette bottles are mounted approximately 0.5 m above the CTD sensors.

Titanium pressure sensors were manufactured by Paine Instrument and were installed with a separate pressure-temperature sensor in both CTDs prior to the cruise. The pressure data has a resolution of 0.1 decibars and an overall accuracy of + 2.0 decibars for CTD# 1100 and + 5.0 decibars for CTD # 2326. The pre-cruise pressure calibration was used for CTD # 1100 while a combination of pre and post cruise pressure calibration was used to process CTD # 2326. The Titanium pressure transducer processing methods follow Millard, et. al (1993). Pressure is calibrated across the pressure sensor's range in the laboratory before and after the cruise. These calibrations are carried out at both room temperature and at the ice point.

The temperature sensor is Rosemount platinum # 171. The fast response temperature thermistor normally employed in the Mark IIIb has been removed. The temperature resolution is 0.0005°C and the accuracy is better than  $\pm 0.0015^{\circ}\text{C}$  (Millard & Yang (1993)) over the range 0 to 30.0°C. Temperature was calibrated in the laboratory before and after the cruise with the CTD instrument fully immersed as described by Millard & Yang (1993). A large (0.01 to 0.015°C) shift of temperature in the same direction was observed to occur with both CTD's 1100 and 2326. This shift was traced to a faulty pre-cruise laboratory temperature standardization. The conductivity sensor is a 3 centimeter alumina cell manufactured by EG&G/NBIS. The resolution of conductivity is 0.001 Ms/cm and the accuracy is directly tied to the water sample salinity accuracy discussed elsewhere in this report. The overall accuracy of the CTD conductivity calibrated to the rosette water bottle salinities is believed to be better than  $\pm 0.0025$  psu.

The CTD oxygen is measured with a plographic sensor manufactured by Sensormedics. The CTD oxygens are calibrated to shipboard Winkler oxygens.

### **2.2. CTD data collection and processing**

The CTD data logging and processing was accomplished on two MSDOS PCs. The data logging was handled on an IBM compatible 80386 system with an 80387 math co-processor. The EG&G data logging program CTDACQ was used to record down and up profiles, separately on disk together with a rosette bottle file. The CTD data was edited to flag spurious data using the EG&G program CTDPOST. The remainder of the CTD post-processing was performed using the WHOI PC-based CTD processing system as described by Millard and Yang (1993). The post-processing was performed on an IBM compatible 80486 system with a 600 Mbyte optical disk (Sony SMO-C501) used for data archiving.

### **2.3. CTD calibration constants**

The standard Alumina conductivity cell materials expansion factors: Alpha = -6.5 E-6, Beta = 1.5 E-8 were applied to CTD #1100 and CTD #2326. When the pre-cruise pressure calibration was applied to CTD 2326 data, a Beta = -1.5 E-8 was required to produce a salinity without a depth dependence; but a combination of pre/post-cruise pressure calibration allowed the use of the standard Beta value. The combined pressure calibration was used to process all CTD #2326 data because it produced CTD salinities free of depth dependence and yielded the pressure bias observed at sea.

**2.4. Pre and post-cruise Laboratory calibrations polynomial coefficients**

$$\text{Eng} = E + Dr + Cr^2$$

(where r is the measured raw CTD data value and Eng is the standard engineering unit of the variable).

The coefficients for each sensor are:

A) Pressure: (Loading/unloading)

CTD #1100

E= -1.075;            D= .108604;            C=0.593893 E-9 pre-cruise

CTD #2326

E= 0.15;            D= .104831;            C= -0.799383 E-9 (pre-cruise)  
 E= -12.5;            D= .105437;            C= -0.752607 E-9 (post-cruise)  
 E= -6.3;            D= .105127;            C= -0.752607 E-9 (pre/post cruise combined)

B) Temperature: (post-cruise)

CTD #1100 (2<sup>nd</sup> order fit, stand. dev. = 0.00035)

E= -0.4055;            D= 0.499576 E-3;            C= 0.13946 E-11 :            Lag= 0.225 s

CTD #2326 (1<sup>st</sup> order fit, stand. dev. = 0.0006)

E= 0.0026;            D= 0.499889 E-3;            Lag= 0.250 s

C) Conductivity:

For CTD #2326 and CTD #1100 conductivity calibrations the post-cruise temperatures were used. For CTD #2326 the data was pressure averaged again after the cruise using the combined pre/post-cruise pressure calibrations while CTD 1100 used the pre-cruise pressure calibration. The conductivity (salinity) calibration was examined closely at the change of instruments during the cruise (i.e. instrument swap outs at stations 62 – 63, 73 – 74, 80 – 81, 88 – 89) and no shifts were found that were not arguably due to oceanic variability.

CTD #1100

This CTD required some fine-tuning of conductivity slope calibrations.

Bias, E= -0.0116 for all the stations

Stations	Slope D=
1 – 62	0.1000 453 E-2
74 (fit to itself)	0.1000 565 E-2
75	0.1000 512 E-2
76	0.1000 510 E-2
77	0.1000 508 E-2
78	0.1000 506 E-2
79	0.1000 505 E-2
80	0.1000 503 E-2
89 – 91	0.1000 500 E-2
92 – 101 (fit to sta. 93 – 95)	0.1000 483 E-2

Stations 96, 97 and 98 salinities are low compared to the water samples, but we believe that water sample salinities are suspect for these stations.

CTD #2326

For this CTD, there is significant down-up hysteresis in one of the salinity sensors (P, T, or C: mostly likely Conductivity). The up-profile salinity is .005 - .007 fresher than the corresponding down-profile at a given potential temperature. Of course, at the bottom of the profile the salinity agrees but by 2.5°C (3500 dbars) on the 6000 dbar profiles a .005 psu discrepancy exists. A program was written to extract and create down-profile conductivity calibration data and we have to refit CTD #2326 conductivities below 2500 dbars.

Stations 63 – 73, bias; E= 0.0083

Station	Slope, D=
63 (Fit to down profile conductivity)	0.1000 2693 E-2
64 (Fit to down profile conductivity)	0.1000 1727 E-2
65	0.1000 1699 E-2
66	0.1000 1671 E-2
67	0.1000 1642 E-2
68	0.1000 1614 E-2
69	0.1000 1585 E-2
70	0.1000 1557 E-2
71	0.1000 1529 E-2
72	0.1000 1500 E-2
73	0.1000 1472 E-2
81 – 88 Bias, E= 0.0121 (01-27-93 calibration)	0.999936 E-3

**Final CTD data edit:**

Two mean profiles were created. One for the West African Basin and a second for the North American Basin, by averaging all deep BIO Hesperides stations on pressure surfaces. These mean profiles have been used to screen the individual casts of each basin for question able temperature, salinity and oxygen data, comparing individual profiles to respective mean profile.

Two edit criteria were used to flag questionable data:

- Temperature, Salinity and Oxygen variations whose difference from the mean profile exceeding 5.5 standard deviations;
- Stability parameter exceeding –1.0E-5 per meter.

A list of stations with bad or questionable data at the surface is given below:

	1	2
W African B.	17, 26, 32, 35, 39, 41, 44, 47	2, 5, 10, 18, 19, 20, 22, 23, 27, 28, 29, 31, 33, 34, 36, 37, 38, 42, 43, 45, 46, 48, 50, 51, 52, 53
N American B.	57, 74, 76, 81	55, 56, 58, 59, 60, 61, 62, 68, 69, 70, 72, 77, 78, 79, 80, 82, 85, 86, 87

1. Stations with bad or too low surface salinities.
2. Stations with questionable surface salinities.

D) Oxygen

The oxygen parameters were adjusted as shown on [tables II and III](#). The header abbreviations denote the following:

- STA= First and last station numbers of the group used for calibration.
- BIAS, SLOPE, PCOR, TCOR, WT, LAG and Edit factor are parameters of the fit as described by Millard and Yang (1993).
- STD DEV= Standard deviation of the fit after some outlying water sample observations are discarded.
- OBS= Number of water sample observations used for the calibration.

**Table II Coefficients for Oxygen Calibrations**

STN	BIAS	SLOPE	PCOR	TCOR	WT	LAG
1-11	.029	.1104e-02	.1664e-03	-.2783e-1	.7510e+00	.7560e+01
12-14	.049	.1139e-02	.1461e-03	-.2990e-1	.7500e+00	.7500e+01
15-19	.031		.1504e-03	-.2939e-1	.8219e+00	.4167e+01
15	“	.1129e-02	“	“	“	“
16	“	.1156e-02	“	“	“	“
17	“	.1158e-02	“	“	“	“
18	“	.1170e-02	“	“	“	“
19	“	.1182e-02	“	“	“	“
20-22	.024	.1197e-02	.1517e-03	-.3090e-1	.7408e+00	.7299e+01
23-31	.032	.1205e-02	.1491e-03	-.3033e-1	.7934e+00	.3211e+01
32-40	.024	.1228e-02	.1501e-03	-.2926e-1	.9210e+00	.7833e+01
41-43	.015	.1233e-02	.1553e-03	-.2998e-1	.7740e+00	.7000e+01
44-46	.006	.1229e-02	.1616e-03	-.3065e-1	.6702e+00	.1623e+02
47-50	.000	.1235e-02	.1673e-03	-.3092e-1	.5287e+00	.2187e+02
51-55	.012	.1226e-02	.1590e-03	-.2953e-1	.8080e+00	.7340e+01
56-62	.032	.1216e-02	.1499e-03	-.2906e-1	.8221e+00	.1549e+02
63-71	-.036	.1256e-02	.1683e-03	-.3041e-1	.7448e+00	.4612e+01
70	“	.1269e-02	“	“	“	“
72-73	-.047	.1338e-02	.1686e-03	-.3241e-1	.6362e+00	.2927e+01
74-80	.027	.1201e-02	.1515e-03	-.2865e-1	.8869e+00	.1027e+02
81-83	-.053	.1276e-02	.1788e-03	-.3177e-1	.6312e+00	.3351e+01
84-87	-.030	.1284e-02	.1645e-03	-.3047e-1	.8147e+00	.1998e+00
88	“	.1320e-02	“	“	“	“
89-101	.039	.1200e-02	.1459e-03	-.2779e-1	.9109e+00	.1390e+02

**Table III Statistics of Adjustments for Oxygen Calibrations**

STN	STD DEV	OBS	STN	STD DEV	OBS
1-11	.7188e-01	59 of 59	47-50	.5274e-01	84 of 91
12-14	.4233e-01	46 of 60	51-55	.5526e-01	83 of 100
15-19			56-62	.3870e-01	116 of 131
15	.6791e-01	19 of 21			
16	.1566e+00	18 of 20	63-71	.5401e-01	176 of 189
17	.5021e-01	19 of 21	70	.7953e-01	22 of 23
18	.3341e+00	21 of 21			
19	.5171e-01	21 of 22	72-73	.8711e-01	45 of 45
20-22	.56355e-01	62 of 67	74-80	.6576e-01	159 of 161
23-31	.6148e-01	189 of 203	81-83	.6388e-01	64 of 66
32-40	.5958e-01	150 of 170	84-87	.7946e-01	72 of 72
			88	.8969e-01	24 of 24
41-43	.7023e-01	68 of 69			
			89-101	.5241e-01	213 of 229
44-46	.4442e-01	68 of 69			

Notes to these tables

- Parameters obtained from stations 7 to 9 apply to stations 1 – 11.
- Stations 15 to 19 were fit fixing parameters of 15 – 21 except slope.
- Stations 32 to 39 calibrations applied to stations 32 to 40.
- Station 70 calibrated as group 63 – 71 except slope
- Station 88 calibrated as 84 – 87 except slope
- Station 89 to 101. Sta. 96 and 98 are excluded in setting calibration parameters. When they were included WT was negative.

Figure 2 shows the histograms for salinity and oxygen differences between CTD and bottle samples deeper than 2500 db.

The mean and standard error for the first one are 1.9 E-4 and 1.3 E-4 respectively. For oxygen, they are 1.1 E-4 and 2 E-3.

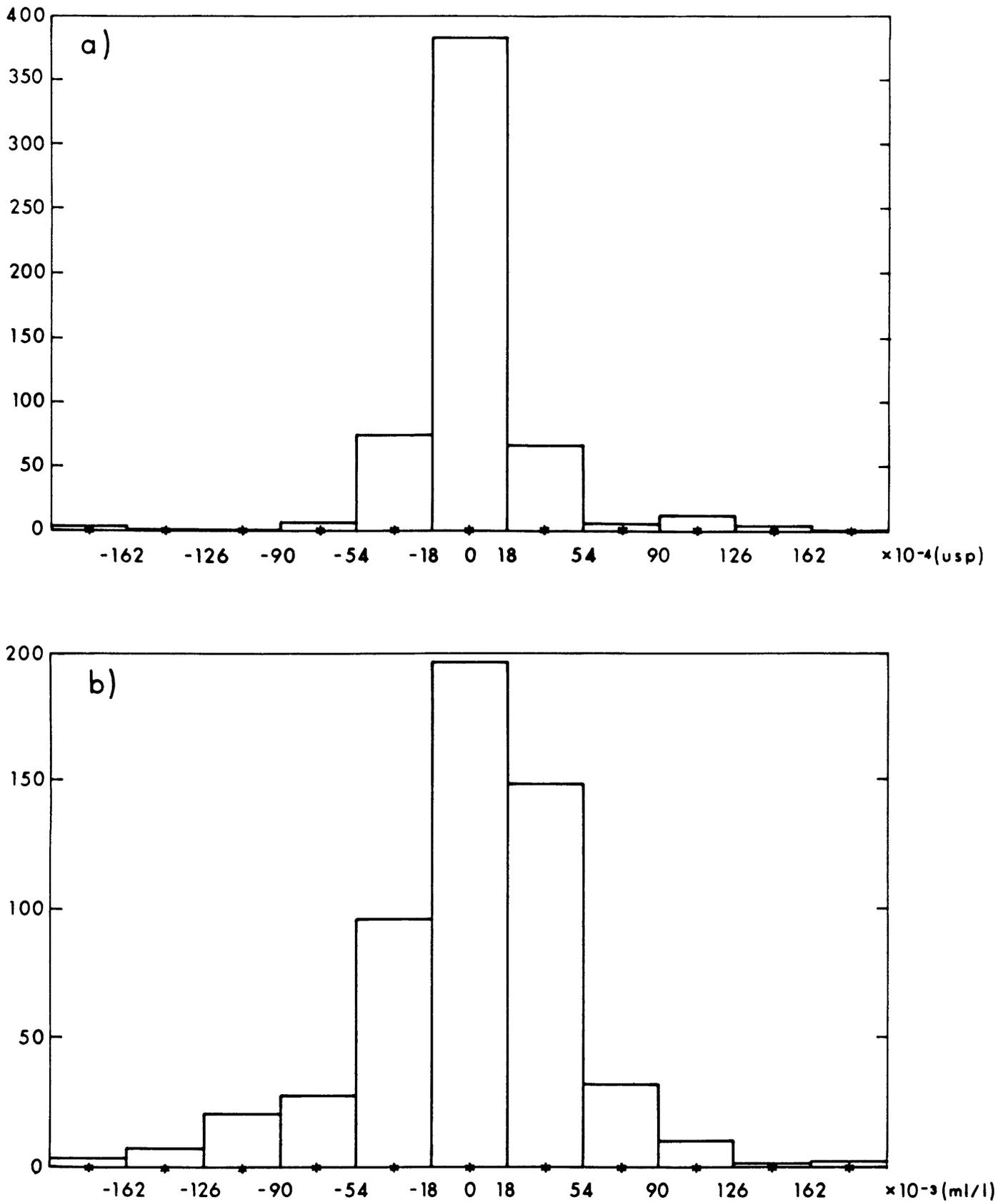


Figure 2: The histograms for a) salinity and b) oxygen differences between CTD and bottle samples deeper than 2500 db.

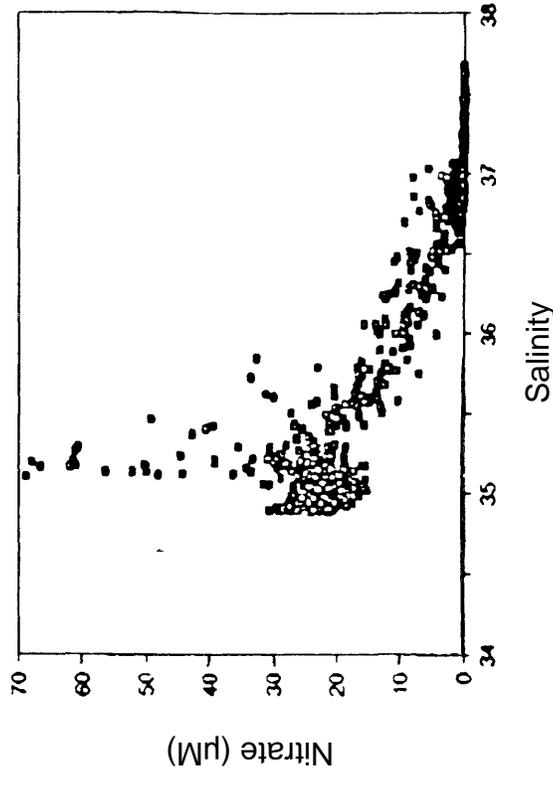
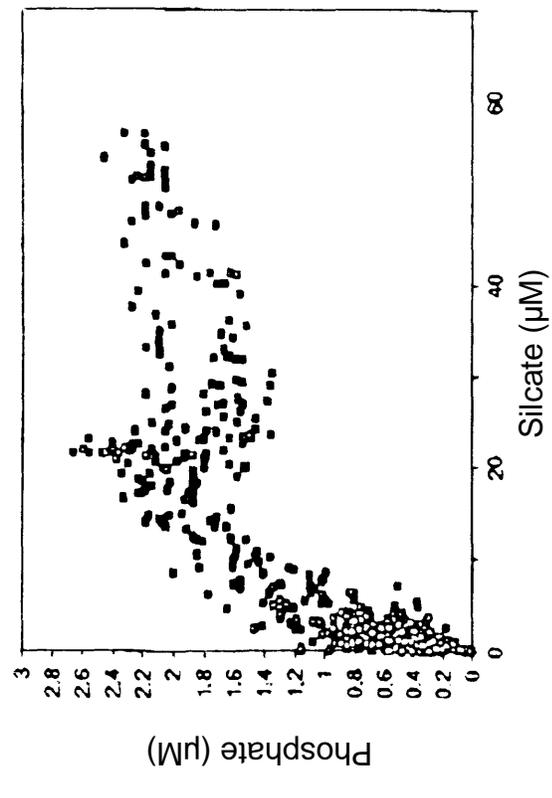
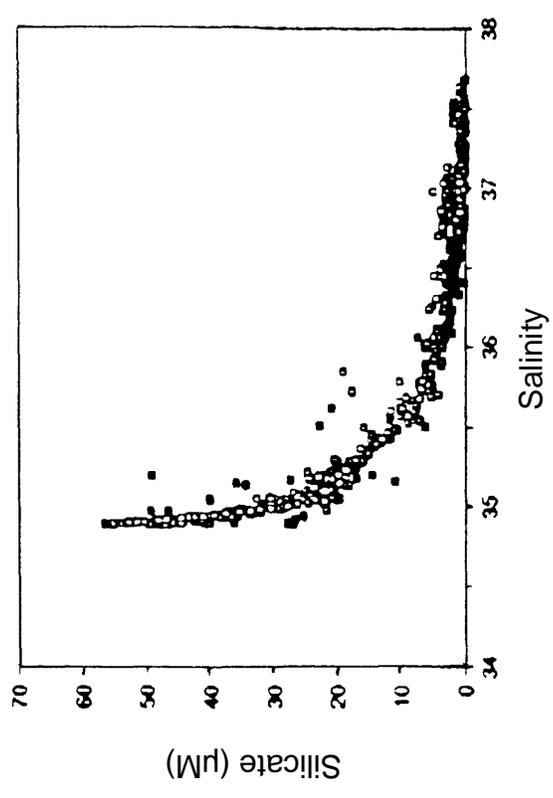
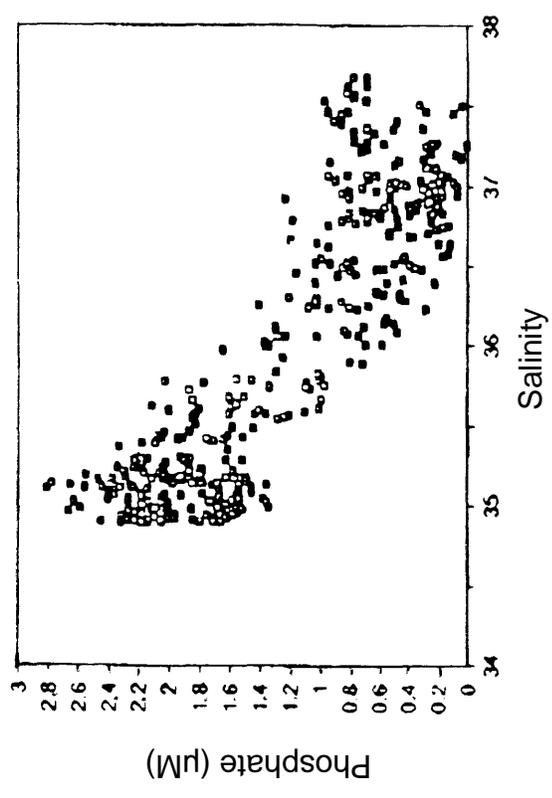


Figure 3: Nutrients diagrams.

### 3. BOTTLE DATA

#### 3.1 Carbon System Parameters

**CARBON DIOXIDE, HYDROGRAPHIC, AND CHEMICAL DATA OBTAINED  
DURING THE *R/V HESPÉRIDES* CRUISE IN THE ATLANTIC OCEAN  
(WOCE SECTION A05, JULY 14 - AUGUST 15, 1992)**

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Environmental Sciences Division  
Publication No- 4988

Date Published: June 2000

Prepared for the  
Environmental Sciences Division  
Office of Biological and Environmental Research  
U.S. Department of Energy  
Budget Activity Numbers KP 12 04 01 0 and KP 12 02 03 0

Prepared by the  
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Oak Ridge, Tennessee 37831-6335  
managed by  
UT-BATTELLE, LLC  
for the  
U.S. DEPARTMENT OF ENERGY  
under contract DE-AC05-00OR22725

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## CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGMENTS

ACRONYMS

ABSTRACT

### PART 1: OVERVIEW

1. BACKGROUND INFORMATION
2. DESCRIPTION OF THE EXPEDITION
  - 2.1 *R/V Hespérides* Cruise Information
  - 2.2 Brief Cruise Summary
3. DESCRIPTION OF VARIABLES AND METHODS
  - 3.1 Hydrographic Measurements
  - 3.2 Carbon Measurements
    - 3.2.1 Methods for Measurement and Computation
    - 3.2.2 Calibrations
    - 3.2.3 Results
4. DATA CHECKS AND PROCESSING PERFORMED BY CDIAC
5. HOW TO OBTAIN THE DATA AND DOCUMENTATION
6. REFERENCES

### PART 2: CONTENT AND FORMAT OF DATA FILES

7. FILE DESCRIPTIONS
  - 7.1 ndp074.txt (File 1)
  - 7.2 stainv.for (File 2)
  - 7.3 a5dat.for (File 3)
  - 7.4 a5sta.dat (File 4)
  - 7.5 a5.dat (File 5)

## LIST OF FIGURES

### Figure

- 1 The cruise track during *R/V Hespérides* Cruise HE06 (WOCE Section A05)
- 2 Sampling depths at all hydrographic stations occupied during *R/V Hespérides* expedition along WOCE Section A05
- 3 Measured values of pH at 25°C vs depth for all stations
- 4 Measured values of total alkalinity (TALK) vs depth for all stations
- 5 Measured values of total carbon dioxide (TCO<sub>2</sub>) vs depth for all stations
- 6 Surface salinity and temperature vs station number
- 7 Surface, total alkalinity (TALK), total carbon dioxide (TCO<sub>2</sub>), and pH vs station number
- 8 Surface values of normalized TALK and TCO<sub>2</sub>, pH at 25°C, and calculated fugacity of CO<sub>2</sub> (*f*CO<sub>2</sub>) vs station number
- 9 Nested profiles: Total carbon dioxide (μmol/kg) vs pressure (dbar) for all stations of WOCE Section A05
- 10 Nested profiles: Total alkalinity (μmol/kg) vs pressure (dbar) for all stations of WOCE Section A05
- 11 Nested profiles pH vs pressure (dbar) for all stations of WOCE Section A05
- 12 Property-property plots for all stations occupied during *R/V Hespérides* Cruise HE06 (WOCE Section A05)

## LIST OF TABLES

### Table

- 1 Summary of the calibration results for the cells at 25°C
- 2 Titrations of certified reference materials (S=33.82) in the laboratory
- 3 Titrations of certified reference materials at sea (Batch #12)
- 4 Summary of carbonate system stations occupied during the cruise
- 5 Content, size, and format of data files

## **ACKNOWLEDGMENTS**

The authors wish to acknowledge the National Oceanographic and Atmospheric Administration, the Oceanographic Section of the National Science Foundation, the U.S. Department of Energy, and the Office of Naval Research for supporting this study.

## ACRONYMS

$^{14}\text{C}$	radiocarbon
ADCP	acoustic Doppler current profiler
A05CII	American Standard Code for Information Interchange
CDIAC	Carbon Dioxide Information Analysis Center
CEAB	El Centro de Estudios Avanzados de Blanes
CFC	chlorofluorocarbon
$\text{CO}_2$	carbon dioxide
CRM	certified reference material
COD	conductivity, temperature, and depth sensor
DOE	U.S. Department of Energy
emf	electromotive force
FCMLP	Facultad de Ciencias del Mar
$f\text{CO}_2$	fugacity Of $\text{CO}_2$
FTP	file transfer protocol
GC	gas chromatography
GMT	Greenwich Mean Time
GO	General Oceanics
GPS	global positioning system
IEO	Instituto Español de Oceanografía
IIM	Institute, de Investigaciones Marinas
IPO	WOCE International Program Office
IR	infrared
JGOFS	Joint Global Ocean Flux Study
LDEO	Lamont-Doherty Earth Observatory
NBIS	Neil Brown Instruments Systems
NDP	numeric data package
nm	nautical mile
NOAA	National Oceanic and Atmospheric Administration
PSS	practical salinity scale
QA	quality assurance
RSMAS	Rosenstiel School of Marine and Atmospheric Science
RTD	resistive temperature device
<i>R/V</i>	research vessel
SIO	Scripps Institution of Oceanography
TALK	total alkalinity
$\text{TCO}_2$	total carbon dioxide
UPC	Universidad Politecnica de Cataluña
URL	universal resource locator
WCRP	World Climate Research Program
WHOI	Woods Hole Oceanographic Institution
WHPO	WOCE Hydrographic Program Office
WOCE	World Ocean Circulation Experiment

## ABSTRACT

Millero, F. J., S. Fiol, D. M. Campbell, G. Parrilla. 2000. Carbon Dioxide, Hydrographic, and Chemical Data Obtained During the *R/V Hespérides* Cruise in the Atlantic Ocean (WOCE Section A05, July 14 - August 15, 1992), L. J. Allison and A. Kozyr (eds.). ORNL/CDIAC-125, NDP-074. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, U.S.A. 51 pp.

This data documentation discusses the procedures and methods used to measure total carbon dioxide (TCO<sub>2</sub>), total alkalinity (TALK), and pH at hydrographic stations during the *R/V Hespérides* oceanographic cruise in the Atlantic Ocean (Section A05). Conducted as part of the World Ocean Circulation Experiment (WOCE), the cruise began in Cadiz, Spain, on July 14, 1992, and ended in Miami, Florida, on August 15, 1992. Measurements made along WOCE Section A05 included COD pressure, temperature, salinity, and oxygen, and bottle salinity, oxygen, phosphate, nitrate, nitrite, silicate, TCO<sub>2</sub>, TALK, and pH.

The TALK, TCO<sub>2</sub>, and pH were determined from titrations of seawater collected at 33 stations. The titration systems for measuring TALK and TCO<sub>2</sub> were calibrated in the laboratory with certified reference materials (CRMs) before the cruise to ensure traceable results. Standard reference seawater provided by Andrew Dickson of Scripps Institution of Oceanography (SIO) was used at sea to monitor the performance of the titration systems. The results agree with the laboratory results to  $\pm 2 \mu\text{mol/kg}$  for TALK and  $\pm 1 \mu\text{mol/kg}$  for TCO<sub>2</sub>. The titration systems used to measure pH were calibrated with TRIS seawater buffers prepared in the laboratory and measured with an H<sub>2</sub>, Pt/AgCl, Ag electrode. The initial electromotive force (emf) of the titrations was used to determine the pH. The values of pH are thought to be reliable to  $\pm 0.01$  and are internally consistent with the measured values of TALK and TCO<sub>2</sub> to  $\pm 7 \mu\text{mol/kg}$ . The measured carbon dioxide system parameters have been used to calculate the in situ values of the fugacity of CO<sub>2</sub> (*f*CO<sub>2</sub>) for the surface water. The surface results are briefly discussed.

WOCE section A05 is located at 24.5°N along the meridional overturn in the Atlantic Ocean. The maximum heat transfer in the North Atlantic Ocean occurs at 24°N; warming in the ocean at this latitude goes down to 3000 m. This section has been studied for a number of years and thus can be used to examine the changes that have occurred in the North Atlantic deep waters. This section has also been studied in the past using inverse methods to look at the movement of CO<sub>2</sub> to and from the North Atlantic.

The WOCE Section A05 hydrographic and carbonate data set is available free of charge as a numeric data package (NDP) from the Carbon Dioxide Information Analysis Center. The NDP consists of two oceanographic data files, two FORTRAN 77 programs, a documentation file, and this printed report, which describes the contents and format of all files as well as the procedures and methods used to obtain the data. Instructions on how to access the data are provided.

**Keywords:** Carbon dioxide; World Ocean Circulation Experiment; North Atlantic Ocean; hydrographic measurements; alkalinity, carbon cycle

## PART 1:

### OVERVIEW

#### 3.1.1. BACKGROUND INFORMATION

There is currently much interest in understanding the inorganic carbon dioxide ( $\text{CO}_2$ ) system in the oceans. This is due to the increasing atmospheric concentration of  $\text{CO}_2$  enhancing the earth-atmosphere system's natural greenhouse effect and potentially affecting the earth's climate. Approximately 40% of the  $\text{CO}_2$  added to the atmosphere as a result of the burning of fossil fuels is thought to be in turn absorbed into the oceans. The flux of carbon dioxide across the air-sea interface is controlled by the difference in the partial pressure of  $\text{CO}_2$  in the atmosphere and in the surface waters. Once the  $\text{CO}_2$  is in solution it can equilibrate with the bicarbonate and carbonate ions. The carbonate ion concentration in the oceans controls the rate of precipitation and dissolution of calcium carbonate ( $\text{CaCO}_3$ ) in the oceans. The carbon dioxide system can be characterized by measuring two of the four measurable parameters [pH, the fugacity of  $\text{CO}_2$  ( $f\text{CO}_2$ ), the total carbon dioxide ( $\text{TCO}_2$ ), and the total alkalinity (TALK)]. The other parameters can be calculated using thermodynamic relations.

To learn more about the role of the world ocean in climate dynamics, several large ocean experiments have been conducted. The World Ocean Circulation Experiment (WOCE) is the largest such experiment ever attempted. A major component of the World Climate Research Program (WCRP), WOCE brings together scientists from more than 30 nations. Although  $\text{TCO}_2$  is not an official WOCE measurement, carbonate chemists are participating in the WOCE cruises as part of the Joint Global Ocean Flux Study (JGOFS) to measure the components of the carbon dioxide system in the oceans. These studies are being sponsored in the United States by the U.S. Department of Energy (DOE) and the National Oceanographic and Atmospheric Administration (NOAA). The carbon dioxide system parameters measured, in order of preference, are the  $\text{TCO}_2$ , TALK, and pH. Preferred analytical methods are coulometry for  $\text{TCO}_2$ , titration for TALK, spectroscopy for pH, and infrared (IR) or gas chromatography (GC) for  $f\text{CO}_2$ . Because coulometry and IR or GC systems to measure  $\text{TCO}_2$  and  $f\text{CO}_2$ , respectively, were not available on the *R/V Hespérides* cruise, and because only one berth was available, the TALK,  $\text{TCO}_2$ , and pH were determined by titration. Although this is not ideal, it was believed that some reasonably precise data were better than no data.

The present report gives the results of carbonate measurements made during the 32 days of the expedition of the *R/V Hespérides* along WOCE section A05 (along 24.5°N) (Fig. 1).

### 3.1.2. DESCRIPTION OF THE EXPEDITION

#### *R/V Hespérides* Cruise Information

Ship name *R/V Hespérides*  
Expedition code 29HE06/1  
WOCE Section A05  
Location Cadiz, Spain; to Santa Cruz de Tenerife, Canary Islands; to Las Palmas de Gran Canaria, Canary Islands; to Miami Florida, U.S.A.  
Dates July 14 - August 15, 1992  
Chief scientist Gregorio Parrilla

<b>Parameters measured</b>	<b>Institution</b>	<b>Principal Investigator</b>
CTD <sup>1</sup>	IEO	G. Parrilla
	WHOI	H. Bryden
Salinity	IEO	R. Molina
Oxygen	IEO	J. Escánez
Nutrients	CEAB	A. Cruzado
Chlorofluorocarbons (CFCs)	LDEO	W. Smethie
pH, TALK, TCO <sub>2</sub>	IIM	A. Rios
	RSMAS	F. Millero
Calcium	IN	G. Roson
Chlorophyll pigments	IEO	J. García Braun
	CEAB	Z. Velazquez
Primary productivity	IEO	J. García Braun
Aluminum	FCMLP	J. Hernández
Radiocarbon ( <sup>14</sup> C)	LDEO	W. Broecker
ADCP <sup>2</sup>	UPC	M. García

<sup>1</sup> Conductivity, temperature, and depth sensor

<sup>2</sup> Acoustic Doppler current profiler.

## Participating Institutions

CEAB	El Centro de Estudios Avanzados de Blanes
FCMLP	Facultad de Ciencias del Mar
IEO	Instituto Español de Oceanografía
IIM	Instituto de Investigaciones Marinas
LDEO	Lamont-Doherty Earth Observatory
RSMAS	Rosenstiel School of Marine and Atmospheric Science
UPC	Universidad Politecnica de Cataluña
WHOI	Woods Hole. Oceanographic Institution

### 3.1.3. Brief Cruise Summary

According to the WOCE Implementation Plan, the cruise line for WOCE Section A05 was to be located at 24°N. Since two oceanographic sections had previously been made (1957 and 1981) around 24.5°N (Roemmich and Wunsch 1985), the WOCE International Program Office (IPO) agreed to a request by the chief scientist to move WOCE Section A05 to this latitude for data comparison purposes.

The *R/V Hespérides* departed from Cadiz, Spain, on July 14, 1992. The cruise track and station locations are shown in [Fig. 1](#). During the cruise, 118 CTD/rosette stations were occupied. Six stations were made to test the CTD and rosette. Four test stations were occupied before the ship arrived at Santa Cruz de Tenerife, Canary Islands, on July 17. The ship left Tenerife on July 18 and occupied two more test stations before arriving at Las Palmas de Gran Canaria. (The data from the six test stations are not included in this NDP.) The ship departed from Las Palmas in the early hours of July 20 and arrived at the first station of WOCE Section A05 the same day. After 101 stations were made, the ship arrived at the Bahamas on August 14 and WOCE Section A05 was completed. During the next day, 11 additional hydrographic stations were collected in the Straits of Florida and the cruise was concluded. For navigation and placement of stations, a global positioning system (GPS) was used.

Because of ship time constraints, station spacing was determined as follows: The first six stations of WOCE Section A05 were located at the 50-, 100-, 150-, 1500-, 2000-, and 2500-m isobaths and were about 18 nautical miles (nm) apart; from there to the 4000-m depth (Station 12), the distance between stations was about 23 nm. From Station 12 to the eastern limits of the Mid-Atlantic Ridge, the stations were separated by 36 nm. Across the Ridge, the separation was 32 nm. From the western limits of the Mid-Atlantic Ridge to the 5000-m isobath near the Bahamas, stations were again separated by 36 nm. Stations close to the Bahamas were separated by less than 30 nm. The stations across the Straits of Florida were occupied every 5 nm.

Near the Bahamas, the expedition deviated slightly from the planned cruise track in order to cross the continental slope perpendicularly to the direction of the isobaths and to obtain a clear crossing of the Deep Western Boundary Current.

The ADCP and a thermosalinograph recorded continuously during the entire cruise. Wind information was recorded every hour. Basic sampling equipment included three CTDs and a 24-bottle General Oceanics (GO) rosette system equipped with 10- or 12-L water sampling bottles

The TCO<sub>2</sub> concentration was determined in 660 samples from 33 of the 112 CTD stations occupied during the cruise ([Fig. 2](#)).

At the end of the cruise the ship was checked for tritium and <sup>14</sup>C contamination by the Tritium Laboratory of the University of Miami.

# Station Number

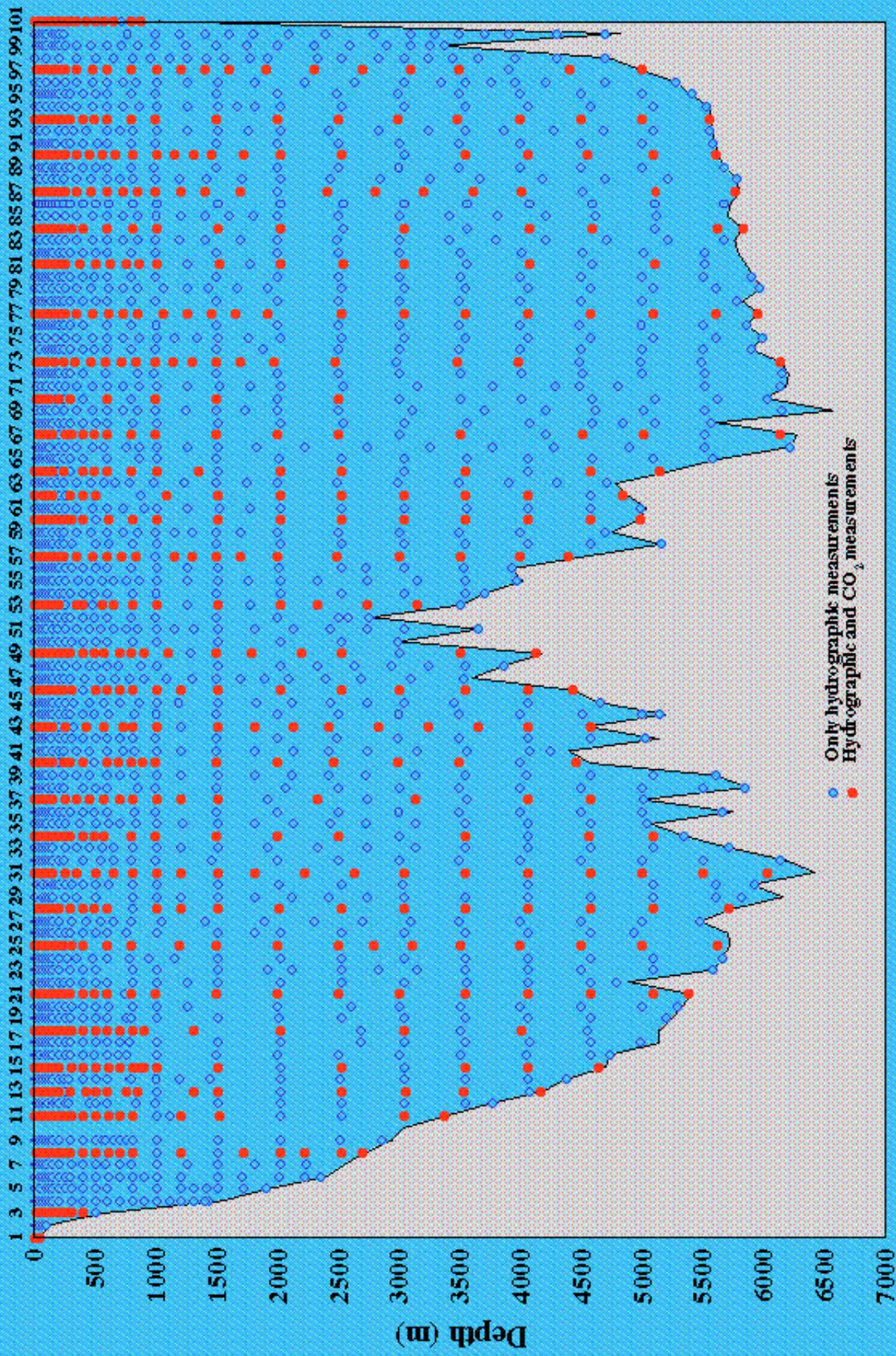


Figure 2: Sampling depths at all hydrographic stations occupied during *R/V Hespérides* expedition along WOCE Section A05

### 3.1.4. DESCRIPTION OF VARIABLES AND METHODS

#### 3.1.4.1. Hydrographic Measurements

The *R/V Hespérides* carried three CTDs, two belonging to the Instituto Español de Oceanografía (IEO) and one belonging to Woods Hole Oceanographic Institution (WHOI). The two EG&G/NBIS Mark IIIb CTD underwater units belonging to IEO were each equipped with pressure, temperature, conductivity, and polygraphic oxygen sensors and were used throughout the cruise. Each CTD was configured identically with the same data scan length, variables, and scanning rate of 31.25 Hz. A detailed description of the Mark IIIb CTD can be found in Brown and Morrison (1978). Both instruments were modified at WHOI to add a titanium pressure sensor with a separately digitized resistive temperature device (RTD) (Millard et al. 1993). The third EG&G/NBIS Mark IIIb CTD was provided by WHOI but was not used during this expedition. A General Oceanics (GO) rosette fitted with 24 10- or 12-L Niskin bottles was used with the CTD for collecting water samples. The GO rosette bottles were mounted approximately 0.5 m above the CTD sensors. The conductivity and oxygen sensors were also calibrated at sea using the analysis of the water samples collected at each station. The depths of the sampling stations were based on classical standard depths, although they varied on a station by station basis according to participants' needs to sample a particular layer, provided there was no impairment of the in situ calibration activities. Because of delays inflicted by Hurricane Andrew on the equipment shipment from Miami to Woods Hole, the post-cruise calibrations were not performed on the CTD sensors until December.

All water sample measurements for bottle salinity and bottle oxygen were made in a constant temperature laboratory soon after each cast was completed. Water samples for salinity were collected from the Niskin bottles in Ocean Scientific International glass bottles, and the measurements were made within 24 hours after the station was finished. In total, 2,294 samples were measured. The bottle salinities were measured with a Guildline Autosal<sup>®</sup> Model 8400A salinometer. The manufacturer claims a precision of 0.0002 and an accuracy of 0.003 when the instrument is operated at a temperature between +4 and -2°C of ambient temperature. All salinity measurements were made in a temperature-control led laboratory about 1-3°C below that of the salinometer water bath.

Bottle oxygen determinations were carried out following the Winkler method and using the reagents prepared according to Carpenter (1965). On this cruise, the modified Carpenter's equation as given by Culberson et al. (1991) was used. The endpoint of titration was determined visually using starch as the indicator. Reagents were dispensed with 0- to 2-ml capacity Dispensette<sup>®</sup> glass and Teflon dispensers from BRAND GMBH & CO. The dispensers had a certified accuracy of ≤0.6% and a coefficient of variation of ≤0.1%. The tips of the dispensers were lengthened up to 6 cm with thin plastic tubing to avoid the precipitation of manganese hydroxide in the neck of sample flasks. Titration was done with a Metrohm Dosimat<sup>®</sup> E.412 automatic burette.

Samples for nutrient analyses (silicate, nitrate, nitrite, and phosphate) were collected in 150-mL acid-rinsed polythene flasks directly from the Niskin bottles, following the protocol established by the WOCE Hydrographic Program. Analyses were performed onboard with a four-channel Skalar, Inc. segmented flow autoanalyzer. Analyses were carried out immediately without any treatment of the samples. When necessary, samples were kept in the cold room (unfrozen and never for more than 10 hours) without additives. The analytical techniques followed were those described by Whitlege et al. (1981) with minor modifications to adapt them to the particular conditions of the instrument used and concentration ranges observed. Primary standards were prepared at the beginning and in the middle of the cruise following Whitlege et al. (1981)- Secondary standards were prepared every two days and preserved with several drops of chloroform in the refrigerator. Running standards of various concentrations were prepared daily, and calibration curves were run at the beginning of each session. Standards were interleaved with unknown samples in order to provide a measure of analytical stability. Whenever changes in sensitivity were noticed (particularly in the case of nitrate), the standards allowed for a correction to be applied. All concentrations were referred to double distilled water prepared by reverse osmosis. No seawater sample has ever given a concentration negative with respect to this double distilled water. Phosphate analyses were corrected for the change in absorbance as a result of the salinity effect. Surface seawater was used as a carrier and, except for silicate, it always showed the minimum concentrations in the water column. Silicate concentrations below the surface were often found to be lower

than those at the surface and very close to the values given by double distilled water. Replicate samples were analyzed at various depths.

More detailed information on hydrographic measurements can be found at:

<http://whpo.ucsd.edu/data/onetime/atlantic/a05/index.htm>.

### 3.1.4.2. Carbon Measurements

The total alkalinity (TALK), total carbon dioxide (TCO<sub>2</sub>), and pH were determined from titrations of seawater collected at 33 stations. The titration systems were calibrated with Dickson standard seawater before and during the cruise. The pH was determined from the initial emf reading relative to TRIS buffers. The results for Dickson samples agree with laboratory spectroscopic measurements for pH to  $\pm 0.005$ .

#### Methods for Measurement and Computation

Three titration systems (Thurmond and Millero 1982) were used to determine the TALK. Each system consisted of a Metrohm 655 Dosimat titrator and an Orion 720A pH meter that was operated by a personal computer (PC) (Millero et al. 1993a). The titration was made by adding HCl to the seawater past the carbonic acid end point (pH $\approx$ 3.5). The solutions were contained in water-jacketed cells (230 cm<sup>3</sup>) controlled to a constant temperature of 25°C with a Forma temperature controller. The computer program used to perform the titration was developed in the Rosenstiel School of Marine and Atmospheric Science (RSMAS) laboratory using RS232 interfaces. A BA05IC program was used to run the titration and record the volume of the added acid and the emf of the electrode system. A typical titration recorded the emf after the readings became stable (0.09 mV) and added enough acid to change the voltage to a pre-assigned value (13 mV). A full titration (25 points) took about 20 minutes. Using two systems, a 24-bottle cast could be analyzed in 4-5 hours.

The electrode systems used to measure the emf of the sample during a titration consisted of a ROSS glass pH electrode and an Orion double-junction reference electrode. A number of electrodes were screened to select those to be used in the titration systems. Electrodes with non-Nernstian behavior (slopes 1.0 mV different from theoretical) in acidic solutions were discarded. The reliability of a glass-reference electrode pair was determined by titrating 0.7-M NaCl solutions with HCl, by using seawater buffers (Ramette et al. 1977), and by determining the TALK of TCO<sub>2</sub>, CRMs provided by Dr. Andrew Dickson of SIO. The titrations of 0.7-M NaCl solutions were used to evaluate the electrode slope in acidic solutions (pH =  $\geq 2$  and  $\geq 4$ ). Seawater buffers (Millero et al. 1993b.) were used to evaluate the electrode slope near a pH of 8. The resulting experimental electrode slopes found for the cells used in the present study are given in Table 1. The slopes near a pH of 8 were lower than the theoretical value (59.16 mV), whereas the slopes near a pH of 3 were near the theoretical value. The electrodes were also evaluated by determining the TALK, TCO<sub>2</sub>, and pH of TCO<sub>2</sub>, CRMs. The results are given in Table 2. The results indicate that precise values of TALK ( $\pm 1.8$   $\mu$ mol/kg), TCO<sub>2</sub> ( $\pm 5$   $\mu$ mol/kg), and pH ( $\pm 0.005$ ) can be obtained on weighed samples of seawater. The precision of the pH measurements for a given electrode (0.003) is better than the average deviation from the mean (0.005).

**Table 1. Summary of the calibration results for the cells at 25°C**

Cell	Volume (CM <sup>3</sup> )	Electrode slope buffer calibration	Standard deviation	Electrode slope acid calibration	Standard deviation
1.00	212.59	58.40	-0.80	59.00	-0.20
6.00	218.50	57.50	-1.70	59.60	0.40
7.00	234.29	58.00	-1.20	59.50	0.30

**Table 2. Titrations of certified reference materials (S = 33.82) in the laboratory**

Seawater	TALK	TCO <sub>2</sub>	pH	N
Batch 12	2227.0 ± 1.8	2002.0 ± 5	7.930 ± 0.01	13
			7.942 ± 0.0005 <sup>a</sup>	
Standard	2226.6	1984	7.940 ± 0.0002 <sup>b</sup>	

<sup>a</sup> Calculated from the initial emf using TRIS buffer calibration.

<sup>b</sup> From spectroscopic measurements.

The HCl acid solutions used throughout the cruise were standardized in the laboratory. The approximately 0.25-M HCl solutions used contained 0.45-M NaCl to yield an ionic strength equivalent to average seawater (0.7 M). Approximately 20 liters of acid were made up in the laboratory. The calibrated acid was stored in 500 cm<sup>3</sup> bottles for use at sea. The acid was standardized by titrating weighed amounts of Na<sub>2</sub>CO<sub>3</sub> and TRIS dissolved in 0.7-M NaCl solution. The blanks in the 0.7-M NaCl solutions were determined by using coulometry and by titrations of the NaCl solutions with and without added Na<sub>2</sub>CO<sub>3</sub> and TRIS. The TCO<sub>2</sub> in the blanks and carbonate solutions was measured daily by a UIC coulometer. The coulometer was calibrated using CO<sub>2</sub> gas loops and CRMs. The blanks of the titrations of TRIS were obtained by extrapolation to zero-added salt. The alkalinity blanks in the NaCl were generally about 14 ± 1 μM. The concentrations of the standard acids obtained from Na<sub>2</sub>CO<sub>3</sub> and TRIS were in good agreement (Millero et al. 1993a).

The volumes of the cells used at sea were determined in the laboratory by weighing the cells filled with water. The density of water at the temperature of the measurements (25°C) was calculated from the international equation of state of seawater (Millero and Poisson 1981). The nominal volumes of all the cells was about 230 cm<sup>3</sup> and the values were determined to +0.03 cm<sup>3</sup>. The reliability of the volumes was assessed by comparing the values of TALK obtained for standard solutions with open and closed cells

A FORTRAN computer program has been developed to calculate the CO<sub>2</sub> parameters (pH<sub>SWS</sub>, emf, TALK, TCO<sub>2</sub> and pK<sub>1</sub><sup>\*</sup>) in Na<sub>2</sub>CO<sub>3</sub> and seawater solutions. These programs are patterned after those developed by Dickson (1984). This program requires an input of the concentration of the acid, the volume of the cell, the salinity, the temperature of analysis, volume of added HCl (V<sub>HCL</sub>), and the corresponding measured values of the emf. To obtain a reliable TALK from a full titration, at least 25 points have to be collected. The precision of the fit is less than 0.4 μmol/kg when pK<sub>1</sub><sup>\*</sup> is allowed to vary, and 1.5 μmol/kg when pK<sub>1</sub><sup>\*</sup> is fixed. This titration program has been compared with the titration programs used by others (Dickson 1981; C. Goyet, WHOI, personal communication, 1992; Bradshaw and Brewer 1988), and the values of TALK agree to within ±1 μmol/kg. Copies of the titration and calculation programs used are available upon request from Frank J. Millero (fmillero@rsmas.miami.edu).

### Calibrations

Before the cruise, a number of titrations were made on CRMs (#12) in the laboratory. The laboratory titration results for TALK, TCO<sub>2</sub>, and pH are given in Table 2 along with the assigned TCO<sub>2</sub> and the pH measured relative to TRIS buffers (Dickson 1993) and spectrophotometrically (Byrne and Breland 1989; Robert-Baldo et al. 1985; Millero et al. 1993b; Clayton and Byrne 1993). It should be pointed out that the values of pH are on the seawater scale defined by Dickson (1984):

$$\text{pH}_{\text{SWS}} = -\log[\text{H}^+]_{\text{SWS}} = -\log\{[\text{H}^+] + [\text{HSO}_4^-] + [\text{HF}]\} \quad (1)$$

The precision in the values of TALK (±2 μmol/kg), TCO<sub>2</sub> (±5 μmol/kg), and pH (±0.005) was quite good. The titration values of TCO<sub>2</sub> were 18 ± 4 μmol/kg higher than the values assigned and measured by coulometry: The titration values of pH (7.93 ± 0.01) were 0.01 lower than the values measured by spectrophotometric methods (7.940 ± 0.002) and using seawater buffers (Millero et al. 1993b). The differences in pH and TCO<sub>2</sub> are caused by the non-ideal behavior of the electrodes near a pH of 8 (Millero et al. 1993a). Calibration of the electrodes using TRIS seawater buffers yielded a pH of 7.942 ± 0.005 from the initial emf readings of the titration. These results are in excellent agreement with the spectrophotometrically determined pH and show a lower standard error than the values determined from the titrations.

The program used to calculate the TCO<sub>2</sub> parameters assumed that the electrodes would respond to a change in pH with an ideal slope of 59.2 mV at 25°C as determined from the Nernst equation. The slopes of the electrodes using buffers and titrating with HCl frequently gave non-ideal behavior. The parameters produced by varying this slope indicated (Millero et al. 1993a) that the deviations resulting from these changes were much greater for TCO<sub>2</sub>, than for TALK. Errors of 1.0 mV in the slope yielded differences in TALK and TCO<sub>2</sub>, respectively, of 2.1 and 22.8 μmol/kg when the pK<sub>1</sub>\* was also allowed to vary (Millero, et al. 1993a). The values of TALK were not strongly affected by the behavior of the electrodes. The values of TCO<sub>2</sub> and pH determined for the CRMs with the buffer-derived slope (58.4) were in good agreement with the correct values (pH = 7.935 and TCO<sub>2</sub> = 1984 μmol/kg). These calculations indicated that the deviations in the TCO<sub>2</sub>, derived from titration were a result of errors in the slope of the electrode, and not a result of unknown protolytes (Bradshaw and Brewer 1988). If the slope determined from the buffers was used, the titrations yielded reliable values of pH, TALK and TCO<sub>2</sub>. This fact was used to make sure that the field titration measurements yielded the Most reliable values of pH and TCO<sub>2</sub>.

During the cruise, the electrodes in each titration system were calibrated with TRIS seawater buffers (Millero 1986) of known pH<sub>SWS</sub> (8.057) determined with a H<sub>2</sub>, Pt/AgCl, Ag electrode (Millero et al. 1993b). Titrations of CRMs (#12) were also made during the cruise. The results are given in Table 3. The average values, TALK = 2229 ± 7 μmol/kg, TCO<sub>2</sub> = 1984 ± 6 μmol/kg, and pH = 7.944 ± 0.01, are in good agreement with the laboratory results. The deviations are larger at sea than obtained in the laboratory (Table 2) but indicate that the titration systems performed well throughout the cruise. The large errors are related to problems in reproducing the volume in the glass cells. Presently, a plastic cell with a more reproducible volume is used, making it possible to reproduce the CRMs to ±2 μmol/kg for TALK, to ±3 μmol/kg for TCO<sub>2</sub>, and to ±0.005 for pH (Millero et al. 1993a).

**Table 3. Titrations of certified reference materials at sea (Batch #12)**

Cell	TALK	TCO <sub>2</sub>	pH	N
1	2229 ± 6	1983 ± 5	7.937 ± 0.009 <sup>a</sup>	14
6	2230 ± 8	1981 ± 8	7.944 ± 0.021 <sup>a</sup>	5
7	2229 ± 6	1984 ± 8	7.948 ± 0.013 <sup>a</sup>	12
Average	2229 ± 7	1984 ± 6	7.942 ± 0.014	31
Standard	2226.6 <sup>b</sup>	1984 <sup>c</sup>	7.940 <sup>d</sup>	

<sup>a</sup> Calculated from the initial emf using TRIS buffer calibration.

<sup>b</sup> Certified value from weighted titrations.

<sup>c</sup> Certified value from manometric extraction technique.

<sup>d</sup> Results obtained in the laboratory using spectrophotometric methods.

## Results

The cruise track of the *R/V Hespérides* is shown in Fig. 1. A summary of the 33 TCO<sub>2</sub> stations that were sampled during the cruise is given in Table 4. Based upon the CRM calibrations at sea, the accuracy of the measured parameters is estimated to be ±7 μmol/kg for TALK and TCO<sub>2</sub> and ±0.02 for pH. The thermodynamic consistency of the measurements can be shown by comparing the calculated values of pH (7.944), TALK (2334 μmol/kg), and TCO<sub>2</sub>, (1984 μmol/kg) using the constants of Roy et al. (1993) with the measured values (Table 3). The agreement is quite good. The values of TALK, TCO<sub>2</sub>, and pH as a function of depth for all of the samples are shown in Figs. 3-5. Plots of the surface properties of the waters sampled are shown in Figs. 6-8.

The temperature increases from 22°C near the Spanish coast to 27°C off the coast of Florida. The salinities go through a maximum (37.5) between stations 20 to 50 (30° to 45° W). The surface values of TALK (Fig. 7) follow this trend. The TCO<sub>2</sub> is fairly constant from stations 1 to 60 (2108 ± 10 μmol/kg) and decreases off the coast of Florida to 2020 μmol/kg. The pH at 25°C increases from 8.05 off the coast of Spain to about 8.12 off the coast of Florida (average pH = 8.05 ± 0.03). The values of TALK and TCO<sub>2</sub>, normalized to S = 35 are shown in Fig. 8. The average normalized TALK is 2293; 4 μmol/kg for the surface waters, whereas the average normalized TCO<sub>2</sub> is 1970 ± 20 μmol/kg. The in situ fugacities of CO<sub>2</sub> (*f*CO<sub>2</sub>) calculated from the measured values of TALK and TCO<sub>2</sub> are shown in Fig. 8. From these

calculations, the surface waters ( $f\text{CO}_2 = 402 \pm 15 \mu\text{atm}$ ) are supersaturated with  $\text{CO}_2$  ( $\Delta f\text{CO}_2 = 42 \pm 15 \mu\text{atm}$ ) for all the surface waters.

**Table 4. Summary of carbonate system stations occupied during the cruise**

Station no.	Latitude ( $^{\circ}\text{N}$ )	Longitude ( $^{\circ}\text{W}$ )	Depth (m)	Date
1	24°29'	15°58'	53	7/20/1992
3	24°29'	16°29'	575	7/20/1992
8	24°29'	18°20'	2736	7/20/1992
11	24°30'	19°35'	3393	7/22/1992
13	24°30'	20°40'	4186	7/23/1992
15	24°30'	21°59'	4705	7/24/1992
18	24°30'	23°59'	5149	7/24/1992
21	24°30'	25°59'	5403	7/25/1992
25	24°30'	28°39'	5723	7/26/1992
28	24°30'	30°38'	5745	7/27/1992
31	24°30'	32°40'	6426	7/28/1992
34	24°30'	34°40'	5354	7/29/1992
37	24°30'	36°40'	5008	7/30/1992
40	24°30'	38°40'	4580	7/30/1992
43	24°30'	40°35'	4551	7/31/1992
46	24°30'	42°20'	4430	8/01/1992
49	24°30'	44°04'	4182	8/01/1992
53	24°30'	46°24°	3518	8/02/1992
57	24°30'	48°44'	4541	8/03/1992
60	24°30'	50°29'	4975	8/04/1992
62	24°30'	51°39'	4888	8/04/1992
64	24°30'	52°50'	5231	8/05/1992
67	24°30'	54°40'	6275	8/05/1992
70	24°30'	56°40'	6024	8/06/1992
73	24°30'	58°39'	6145	8/07/1992
77	24°30'	61°19'	5965	8/08/1992
81	24°30'	63°59'	5858	8/09/1992
84	24°30'	65°59'	5832	8/10/1992
87	24°30'	68°00'	5805	8/11/1992
90	24°30'	70°00'	5626	8/12/1992
93	24°30'	71°59'	5571	8/12/1992
97	25°00'	74°20'	4994	8/13/1992
101	24°30'	75°31'	1040	8/14/1992

### 3.1.5. DATA CHECKS AND PROCESSING PERFORMED BY CDIAC

An important part of the NDP process at the Carbon Dioxide Information Analysis Center (CDIAC) involves the quality assurance (QA) of data before distribution. Data received at CDIAC are rarely in a condition that would permit immediate distribution, regardless of the source. To guarantee data of the highest possible quality, CDIAC conducts extensive QA reviews that involve examining the data for completeness, reasonableness, and accuracy. The QA process is a critical component in the value-added concept of supplying accurate, usable data for researchers. The following information summarizes the data processing and QA checks performed by CDIAC on the carbon-related, hydrographic, and chemical data obtained during the *R/V Hespérides* cruise along WOCE Section A05 in the Atlantic Ocean.

1. Carbon-related data and hydrographic measurements were provided to CDIAC by Frank Millero (RSMAS). The final hydrographic and chemical measurements and the station information files were provided by the WOCE Hydrographic Program Office (WHPO) after quality evaluation. A FORTRAN 77 retrieval code was written and used to merge and reformat all data files.
2. To check for obvious outliers, 0 data were plotted using a PLOTNEST.C program written by Stewart C. Sutherland (Lamont-Doherty Earth Observatory). The program plots a series of nested profiles, using the station number as an offset; the first station is defined at the beginning, and subsequent stations are offset by a fixed interval (Figs. 9-11). Several outliers were identified and marked with the quality flags of “3” (questionable measurement) or “4” (bad measurement) (see File Descriptions in Section 7 of this documentation).
3. To identify "noisy" data and possible systematic, methodological errors, property -property plots for all parameters were generated (Fig. 12), carefully examined, and compared with plots from previous expeditions in the Atlantic Ocean.
4. All variables were checked for values exceeding physical limits, such as sampling depth values greater than the given bottom depths.
5. Dates, times, and coordinates were checked for bogus values (e.g., values of MONTH < 1 or > 12; DAY < 1 or > 31; YEAR < or > 1992; TIME < 0000 or > 2400; LAT < 20.000 or > 30.000; and LONG < -90.000 or > 0.000).
6. Station locations (latitudes and longitudes) and sampling times were examined for consistency with maps and cruise information supplied by Frank J. Millero of RSMAS.
7. The designation for missing values, given as -9.0 in the original files, was changed to -999.9 for consistency with other oceanographic datasets.

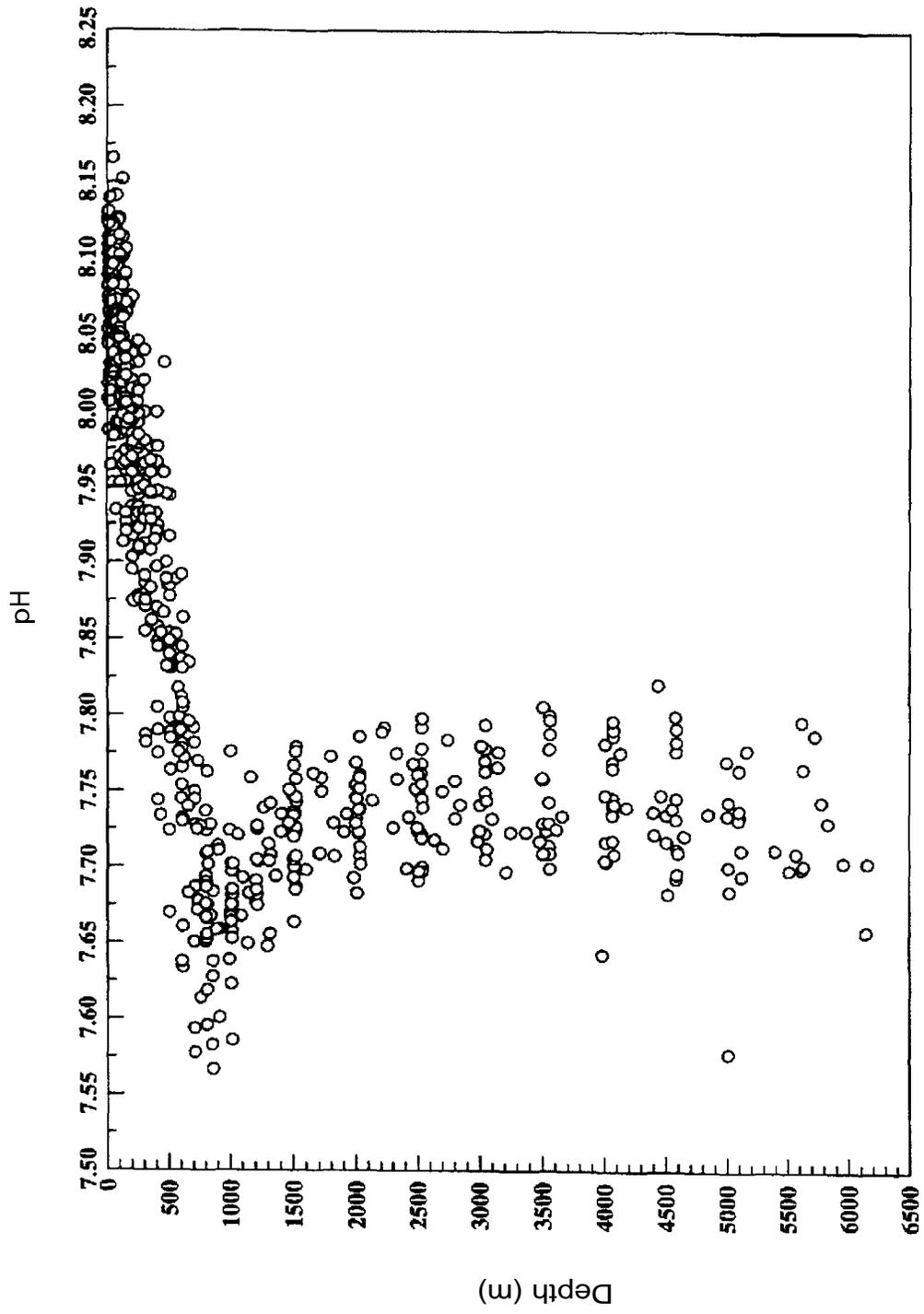


Figure 3: Measured values of pH at 25°C vs depth for all stations

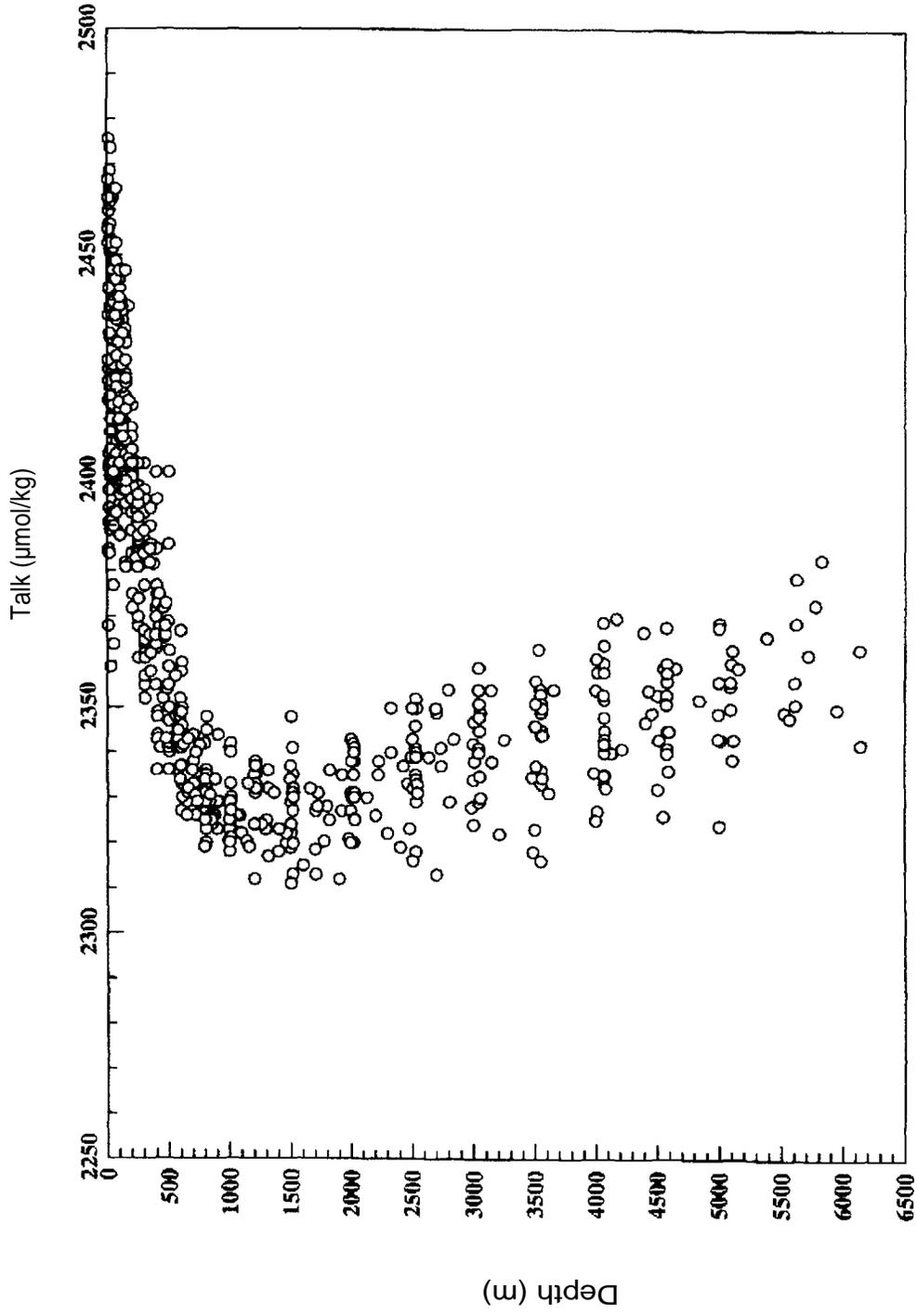


Figure 4: Measured values of total alkalinity (TALK) vs depth for all stations

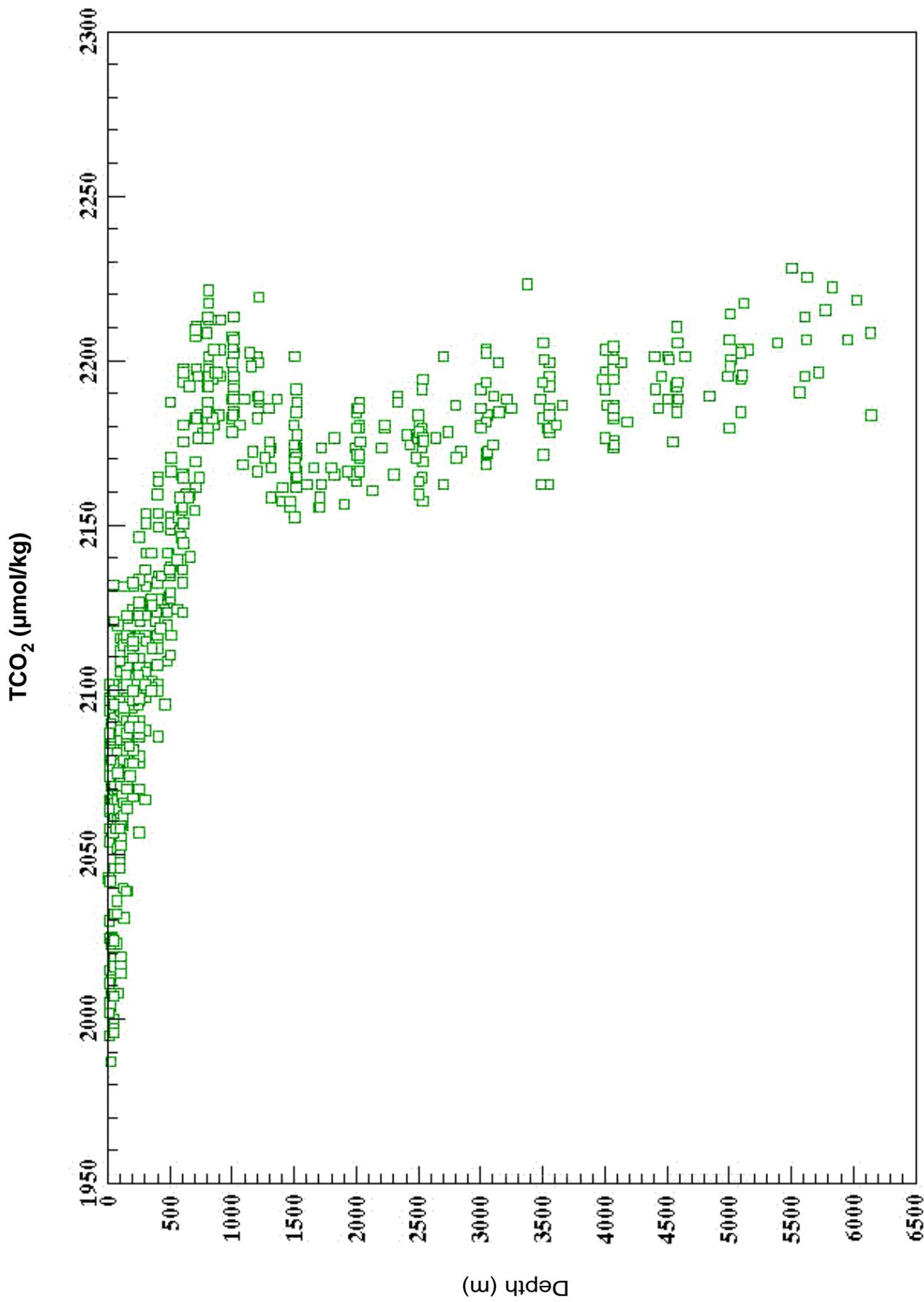


Figure 5a: Total carbonate according to the depth for all the stations in which it was measured.

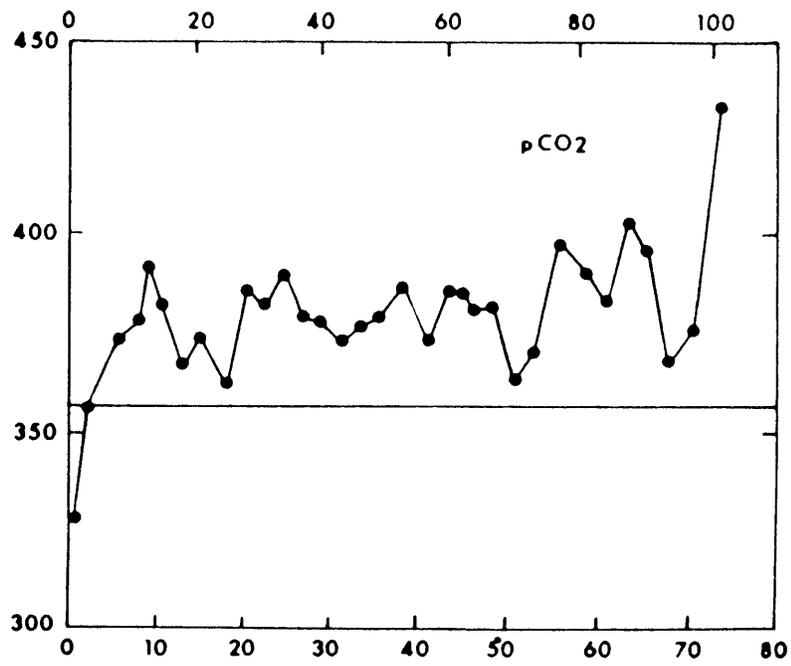


Figure 5b: Calculated pressure of CO<sub>2</sub> throughout the passage of the cruise.

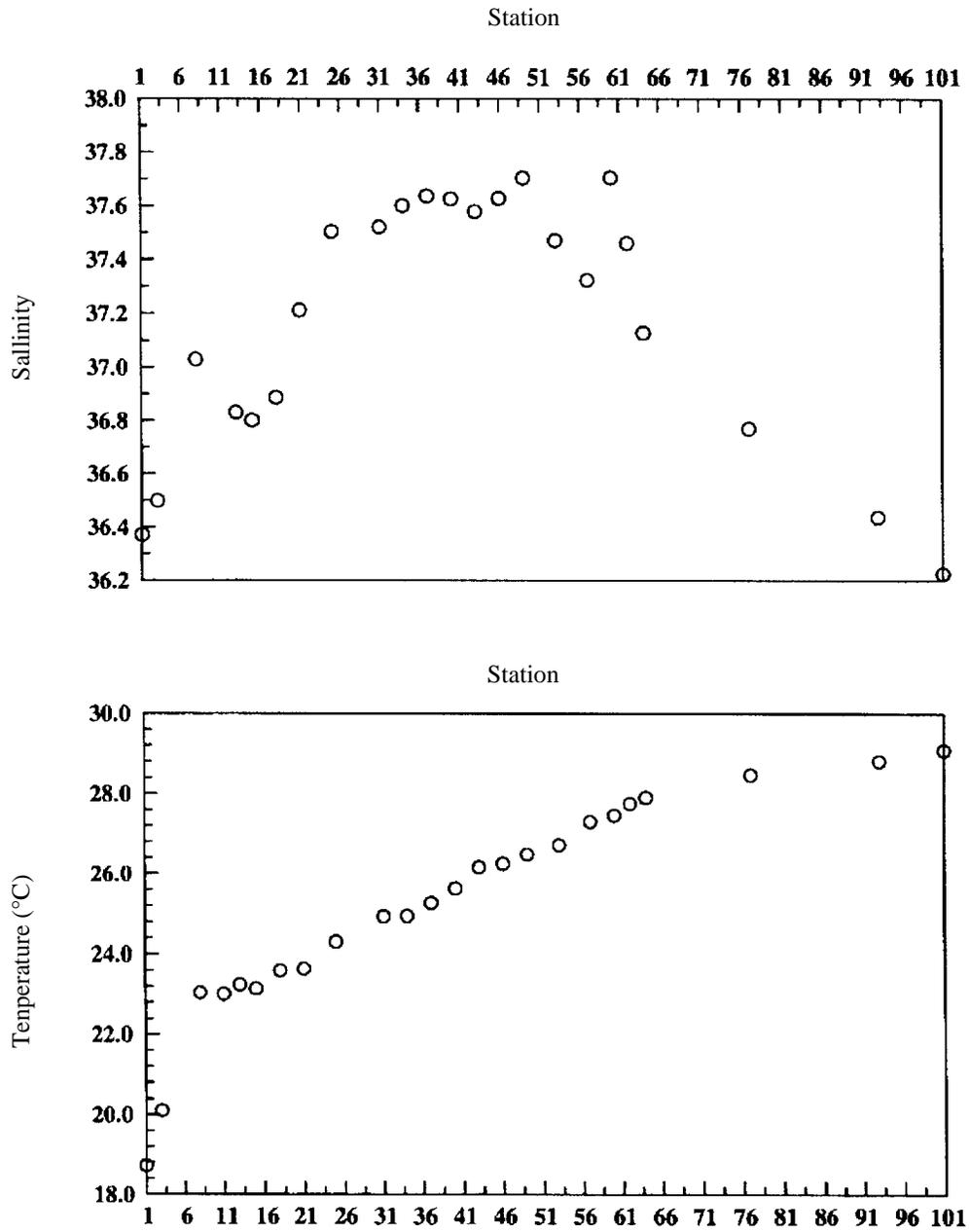


Figure 6: Surface salinity and temperature vs station number

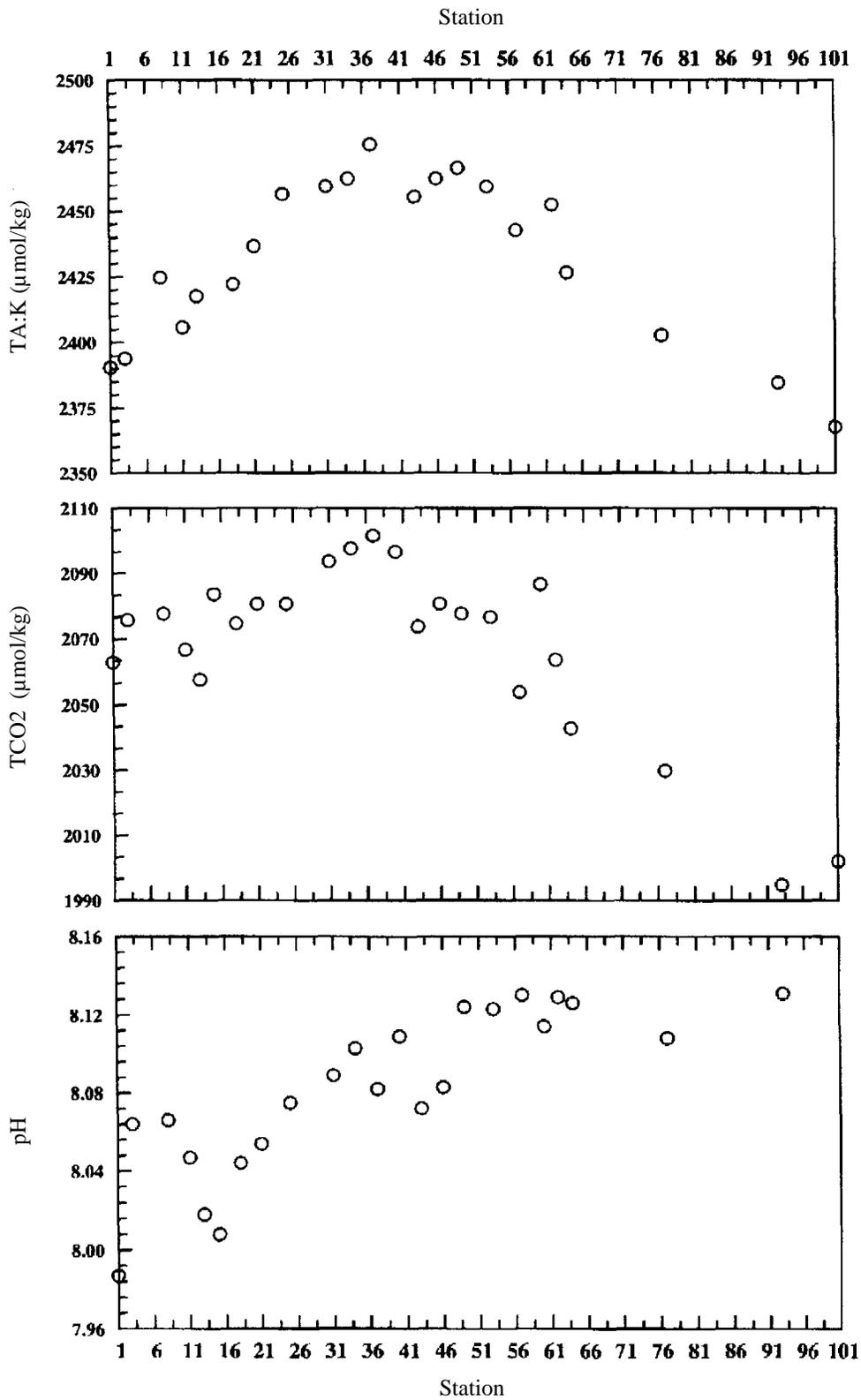


Figure 7: Surface, total alkalinity (TALK), total carbon dioxide (TCO<sub>2</sub>), and pH vs Station number

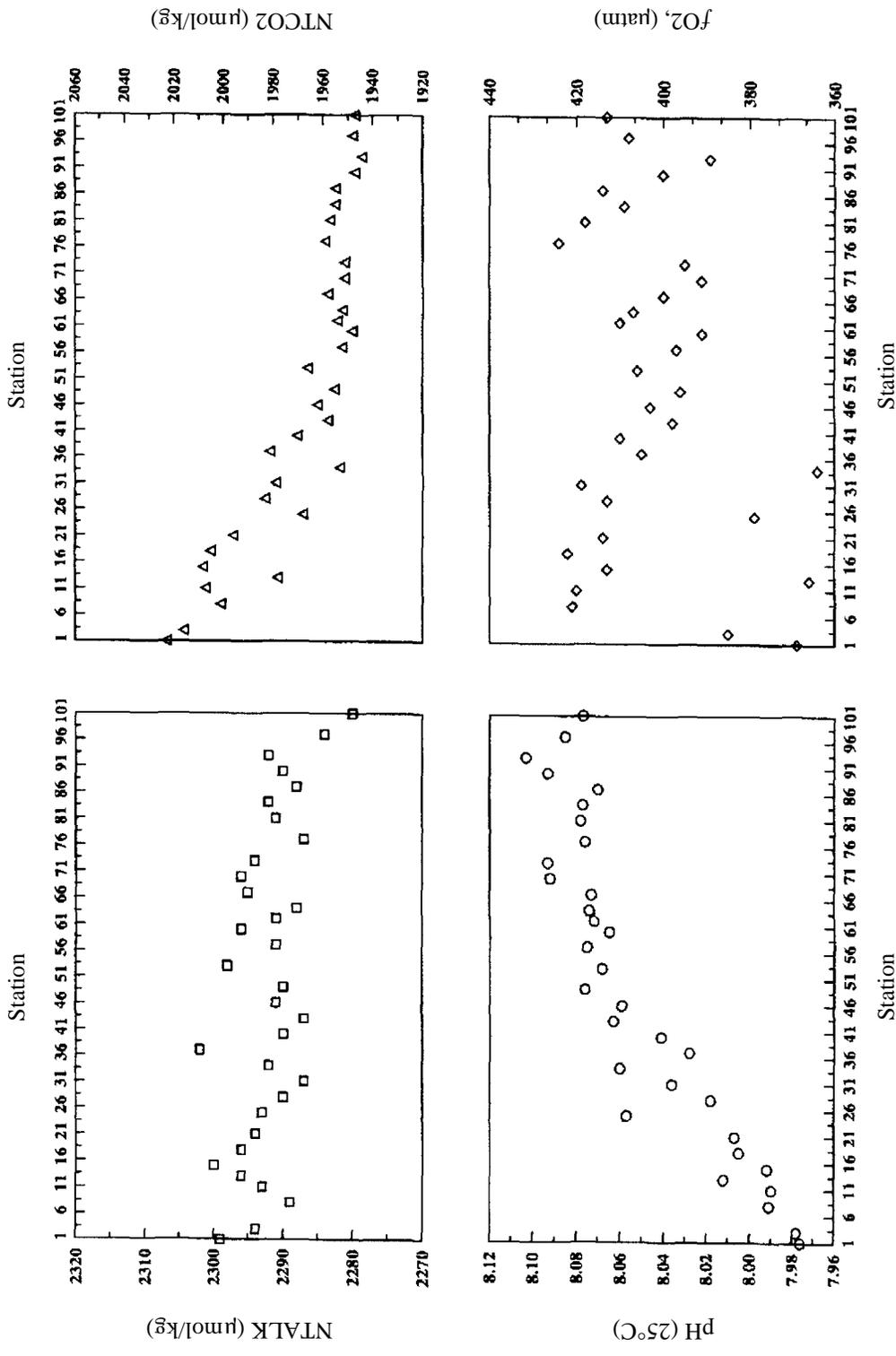
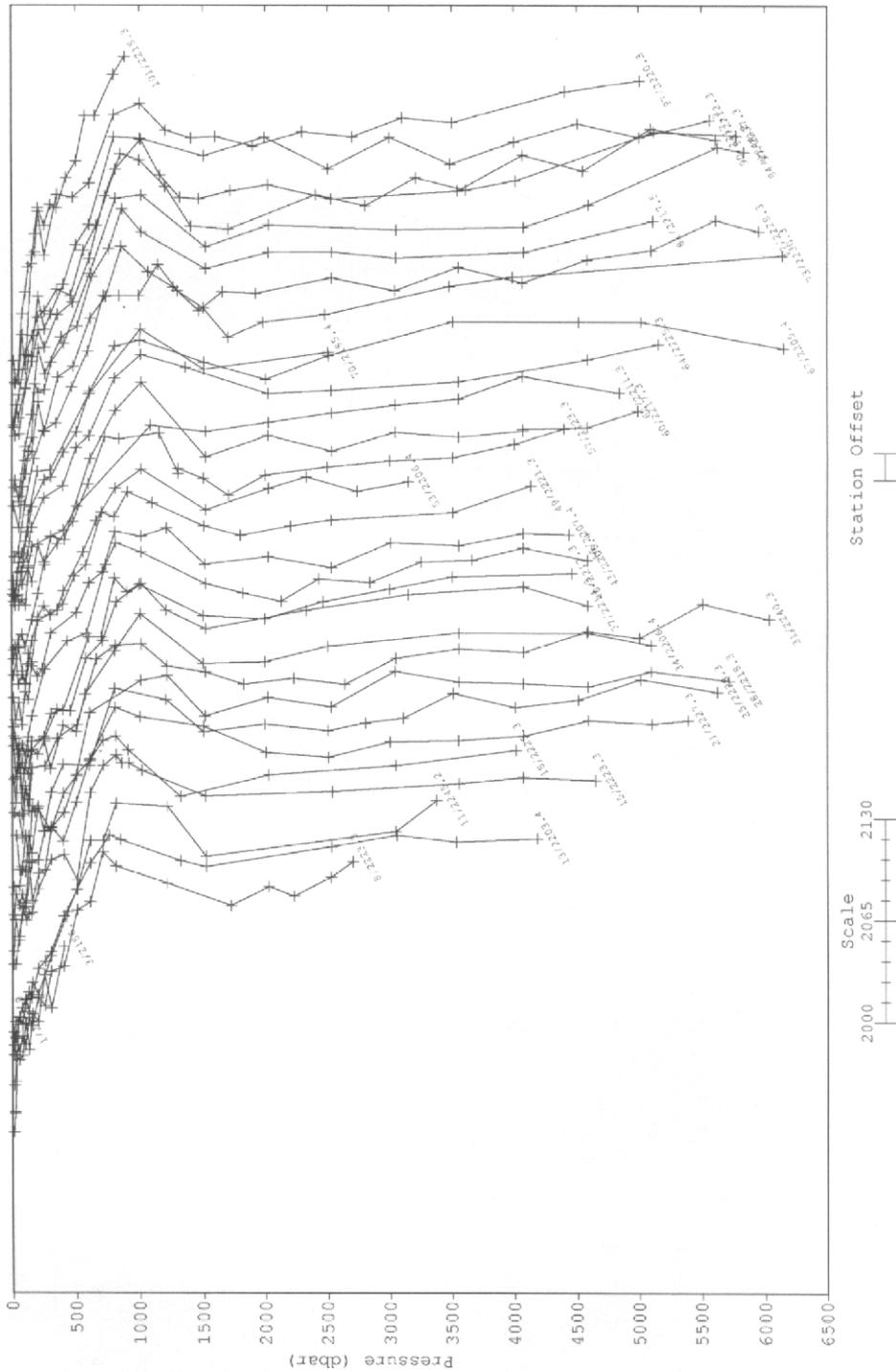


Figure 8: Surface values of normalized TALK and TCO<sub>2</sub>, pH at 25°C, and calculated fugacity of CO<sub>2</sub> ( $f\text{CO}_2$ ) vs station number.

**WOCE Section A5  
Total CO2 (all stations)**

Only profiles which exist in this Pressure (dbar) range are plotted.  
Plotted parameter ranges from 2000 to 2260



**Fig. 9. Nested profiles: Total carbon dioxide ( $\mu\text{mol/kg}$ ) vs pressure (dbar) for all stations of WOCE Section A5.**

WOCE Section A5  
Total Alkalinity (all stations)

Only profiles which exist in this Pressure (dbar) range are plotted.  
Plotted parameter ranges from 2300 to 2500

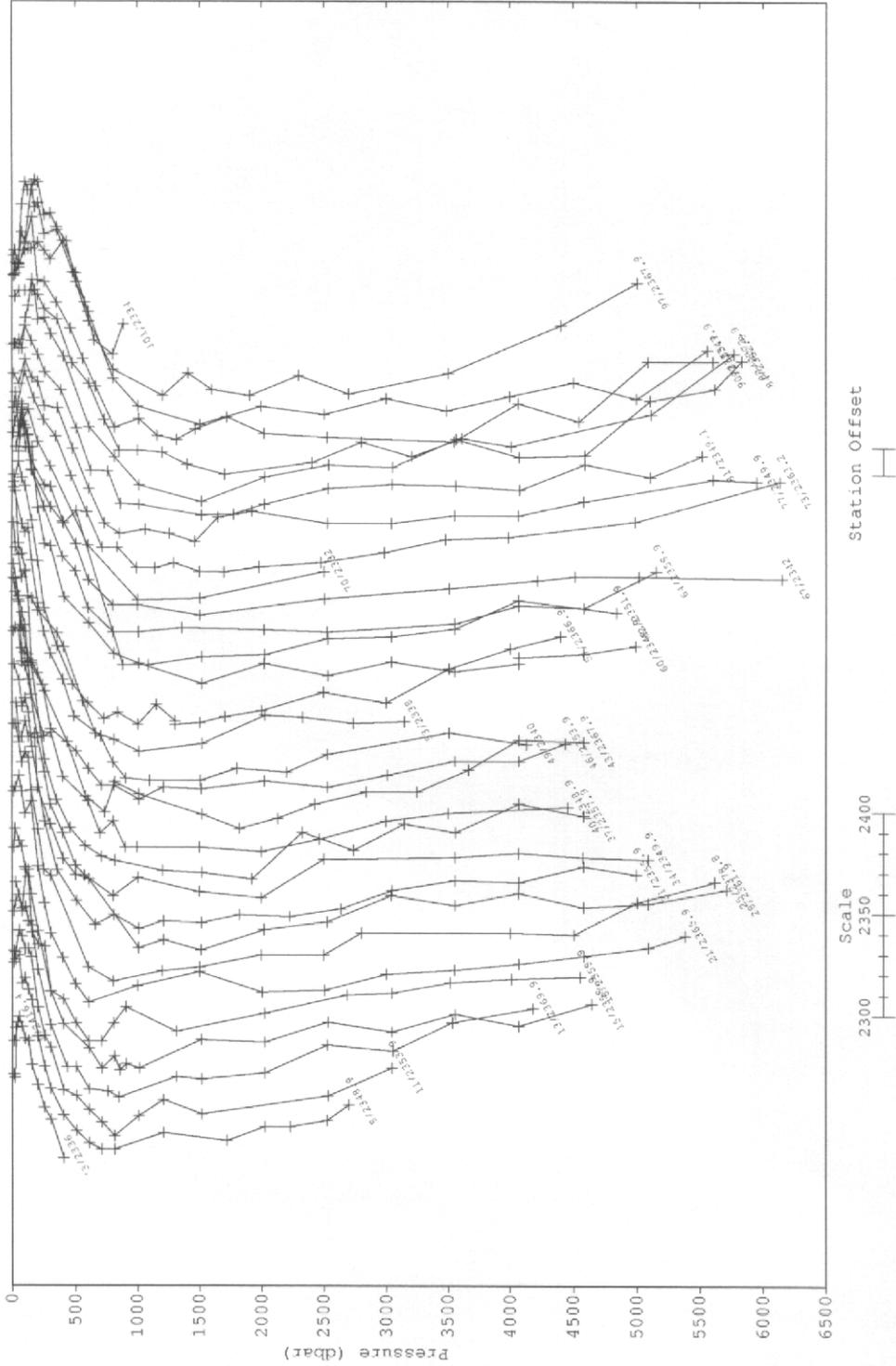
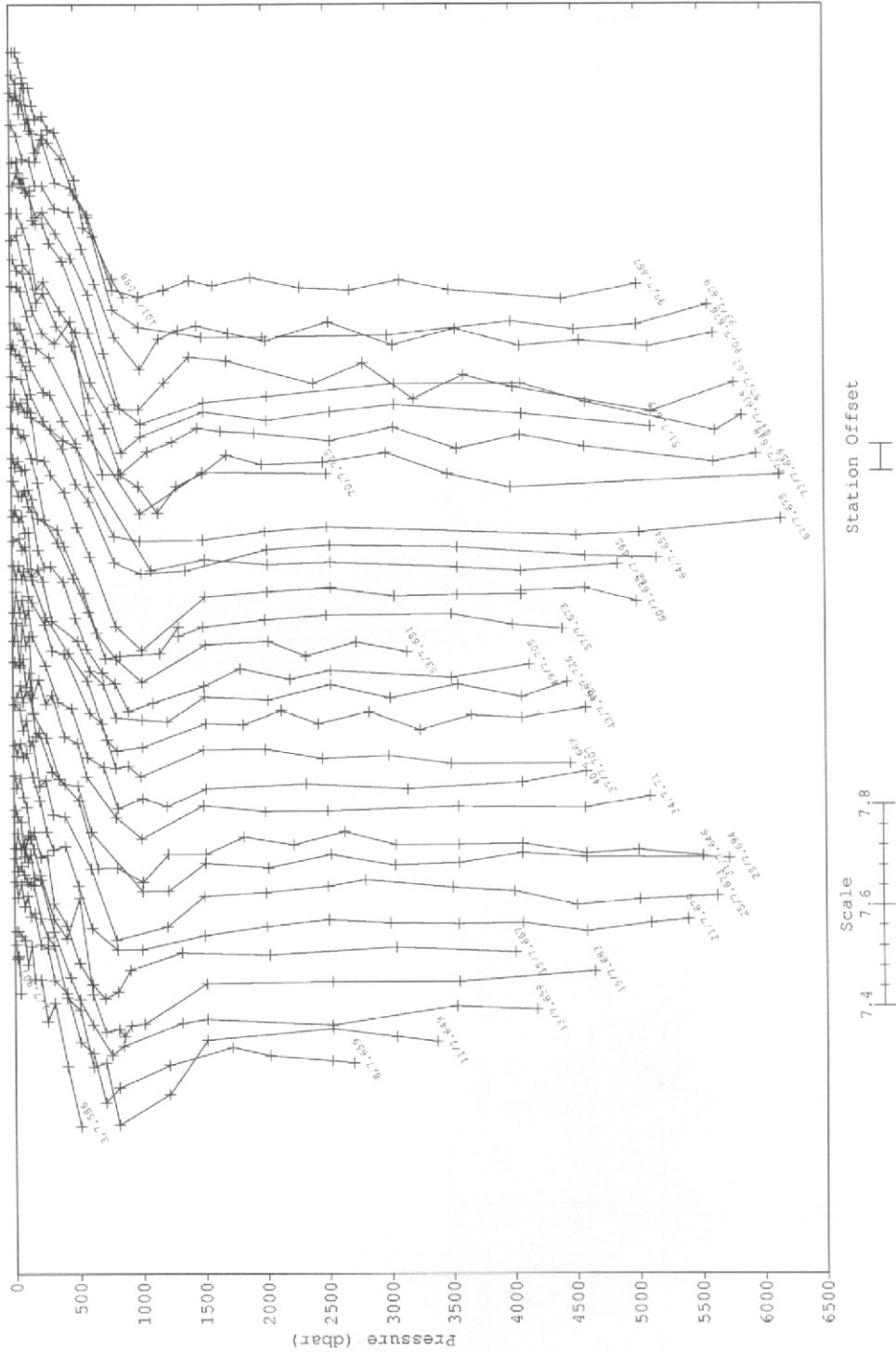


Fig. 10. Nested profiles: Total alkalinity (µmol/kg) vs pressure (dbar) for all stations of WOCE Section A5.

**WOCE Section A5  
pH (all stations)**

Only profiles which exist in this Pressure (dbar) range are plotted.  
Plotted parameter ranges from 7.4 to 8.2



**Fig. 11. Nested profiles: pH vs pressure (dbar) for all stations of WOCE Section A5.**

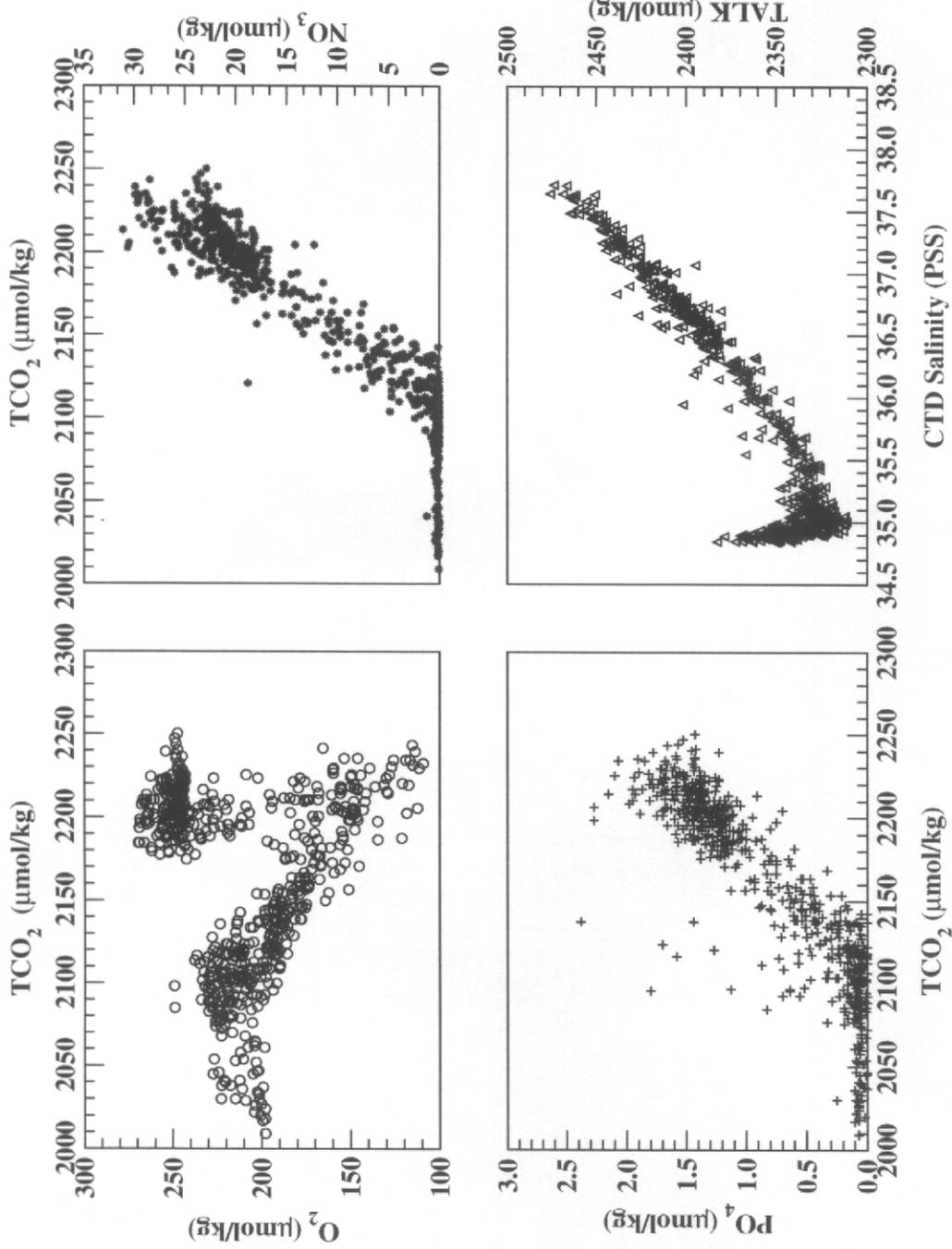


Fig. 12. Property-property plots for all stations occupied during R/V Hespérides Cruise HE06 (WOCE Section A5).

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### 3.1.6. HOW TO OBTAIN THE DATA AND DOCUMENTATION

This database (NDP-074) is available free of charge from CDIAC. The complete documentation and data can be obtained from the CDIAC oceanographic Web site (<http://cdiac.esd.ornl.gov/oceans/doc.html>), through CDIAC's online ordering system (<http://cdiac.esd.ornl.gov/pns/how-order.html>), or by contacting CDIAC. The data are also available from CDIAC's anonymous file transfer protocol (FTP) area via the Internet. Please note that your computer needs to have FTP software loaded on it (this is built in to most newer operating systems). Use the following commands to obtain the database.

```
ftp cdia.esd.ornl.gov or >ftp 128.219.24.36 Login. "anonymous" or "ftp" Password: your e-mail address ftp> cd
pub/ndp074/ ftp> dir ftp> mget (files) ftp> quit
```

Contact information:

Carbon Dioxide Information Analysis Center  
Oak Ridge National Laboratory  
P.O. Box 2008  
Oak Ridge, Tennessee 37831-6335  
U.S.A.

Telephone: 865-574-3645  
Telefax: 865-574-2232

E-mail: [cdiac@ornl.gov](mailto:cdiac@ornl.gov)  
Internet: <http://cdiac.esd.ornl.gov/>

### 3.2 Salinity (R. Molina)

For the salinity measurements the recommendations given in the training Course Notes (Ocean Scientific Int., Funchal, July 1991) were followed. The water sample salinities were measured with a Guildline Autosol Model 8400A salinometer. The manufacturer claims a precision of 0.0002 and an accuracy of 0.003 when the instrument is operated at a temperature between +4° and -2°C of ambient temperature. All the salinity measurements were made in a temperature controlled laboratory about 1° to 3°C below that of the salinometer water bath.

Two different batches of standard water were used: batch P120 (April 6, 1992) with 50 ampoules and 20 ampoules from batch P117 (July 10, 1991). After the salinometer was standardised with water from the first batch, 8 samples from an ampoule of the second batch were measured, and the labelled value of 34.994 was obtained within  $2 \times 10^{-5}$ . On the average, the salinometer was standardised every 31 samples.

Water samples were collected from the Niskin bottles in Ocean Scientific International glass bottles and the measurements were made within the 24 hours after the station was finished. In total 2294 samples were measured.

In determining the conductivity ratio, three measurements were made from every sample providing the differences were smaller than  $2 \times 10^{-5}$ . If not, more measurements were made until three consecutive values exhibited differences smaller than  $2 \times 10^{-5}$ .

In 3 stations, samples were replicated with the following results:

Sta.	Depth	Bottle no.	No. of Samples	Standard dev.
50	2500	02, 3, 4, 5, 6, 7	6	$\pm 3.6 \times 10^{-4}$
64	2532	6	8	$\pm 1.3 \times 10^{-4}$
72	249	16	8	$\pm 2.1 \times 10^{-4}$

During one day when the air conditioning of the laboratory broke down, salinity measurements for stations 2 to 3 were made with the laboratory temperature 0.3°C above the salinometer bath temperature.

### 3.3 Oxygen (J. Escáñez)

Oxygen determinations were carried out following the Winkler method and using the reagents prepared according to Carpenter (1965). We used the modified Carpenter's equation as given by Culberson et al (1991). The endpoint of titration was determined visually using starch as indicator.

Reagents were dispensed with all glass and Teflon dispensers "Dispensette" from Brand GMBH and Co. (0-2 ml capacity) with certified accuracy of  $\pm 0.6\%$  and a coefficient of variation of  $\pm 0.1\%$ . The tips of the dispensers were lengthened up to 6 cm with thin plastic tubing to avoid the precipitation of manganese hydroxide in the neck of sample flasks.

Titration was done with a Metrohm Dosimat E.412 automatic burette using Potassium Iodate "pro.anlysi" Merck (Lot N° 150 BZ 252853. Assay 99.95 – 100.05%) at a concentration of 0.0100 N.

Standards and blanks were dispensed with class "A" calibrated hand pipets with certified accuracy of  $\pm 0.02$  ml for 10 ml pipets and  $\pm 0,006$  ml for 1 ml pipets.

In total, 2338 samples were taken (Table IV). In order to assess good quality results, calibration sets were run through 7 stations. Inter-sample calibrations were run on 3 stations by taking 1 sample from 6 Niskin bottles triggered at the same depth, while on 4 stations intra-samples calibrations were performed taking 6 samples of 2 Niskin bottles triggered at the maximum and minimum O<sub>2</sub> layers respectively. Values are shown in Tables V and VI.

**Table IV**      **Distribution of Casts/Analysts**

<b>Analysts</b>	<b>Station Casts</b>	<b>Stations Analyzed</b>	<b>No. of Samples Analyzed</b>
J.G. Braun	36	11	234
B. Amengual	38	20	446
J. Escáñez	38	81	1658

**Table V** **Calibrations between Casts**

<b>STN</b>	<b>DEPTH</b>	<b>BOTTLE NO.</b>	<b>O<sub>2</sub> (ml/l) Mean</b>	<b>O<sub>2</sub> (ml/l) Std. Dev.</b>
1	40 m	12, 13, 14, 15, 17	X= 5.711	sd=± 0.009
1	40 m	1, 2, 3, 4, 5, 6	X= 4.661	sd= ± 0.031
50	2500 m	2,3,4,5,6,7	X= 5.655	sd= ± 0.005
107	378 m	3,4,5,6,7,8	X= 2.998	sd= ± 0.005

**Table VI**      **Calibrations within Casts (Maximum and Minimum)**

<b>STN</b>	<b>BOTTLE NO.</b>	<b>MAX/MIN O<sub>2</sub></b>	<b>O<sub>2</sub> (ml/l) Mean</b>	<b>O<sub>2</sub> (ml/l) Std. Dev.</b>
14	1	Max	X= 5.601	sd= ± 0.015
14	10	Min	X= 2.575	sd= ± 0.003
32	8	Max	X= 5.622	sd= ± 0.002
32	12	Min	X= 3.294	sd= ± 0.014
67	6	Max	X= 5.907	sd= ± 0.009
67	12	Min	X= 3.513	sd= ± 0.002
89	5	Max	X= 6.193	sd= ± 0.003
89	11	Min	X= 3.469	sd= ± 0.005

### 3.4.      **Nutrients** (A. Cruzado)

Analyses were performed on board with a four channel SKALAR segmented flow autoanalyzer. Samples were collected in 150 ml acid-rinsed polythene flasks directly from the Niskin bottles, following the protocol established by the WOCE Hydrographic Programme. Analyses were carried out immediately without any treatment of the samples. When necessary, samples were kept in the cold room (unfrozen and never for more than 10 hours) without additives.

The analytical techniques followed were those described by Whitley et al. (1981) with minor modifications to adapt them to the particular conditions of the instrument used and concentration ranges observed. Primary standards were prepared at the beginning and in the middle of the cruise prepared every two days and preserved with some drops of chloroform in the fridge. Running standards were interleaved with unknown samples in order to provide a measure of analytical stability. Whenever changes in sensitivity (particularly in the case of nitrate) were noticed, these standards allowed for a correction to be applied.

All concentrations were referred to double distilled water prepared by reverse osmosis through milliRo, dionization through Milli-Q and distillation. No sea water sample has ever given a concentration negative with respect to this double distilled water. Phosphate analysis corrected for the change in absorbance due to the salinity effect. Surface seawater was used as carrier and, except for silicate, it always showed the minimum concentrations in the water column.

Silicate concentrations below the surface were often found to be lower than the surface values and very close to the values given by double distilled water. Replicate samples were analyzed at various depths both from the same and from different Niskin bottles. A comparison of all the primary and secondary standards used during the cruise is underway and may introduce some small corrections to the results. A statistical assessment of such analyses is being prepared. Some nutrient diagrams are shown in [figure 13](#).

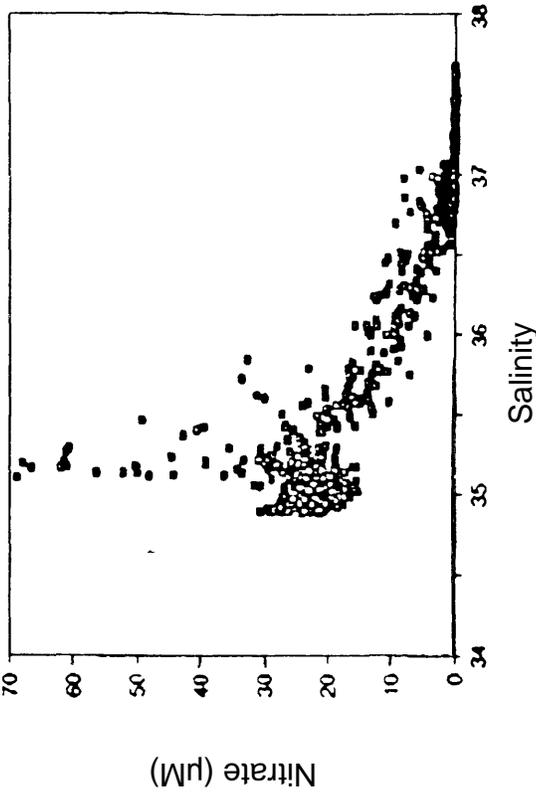
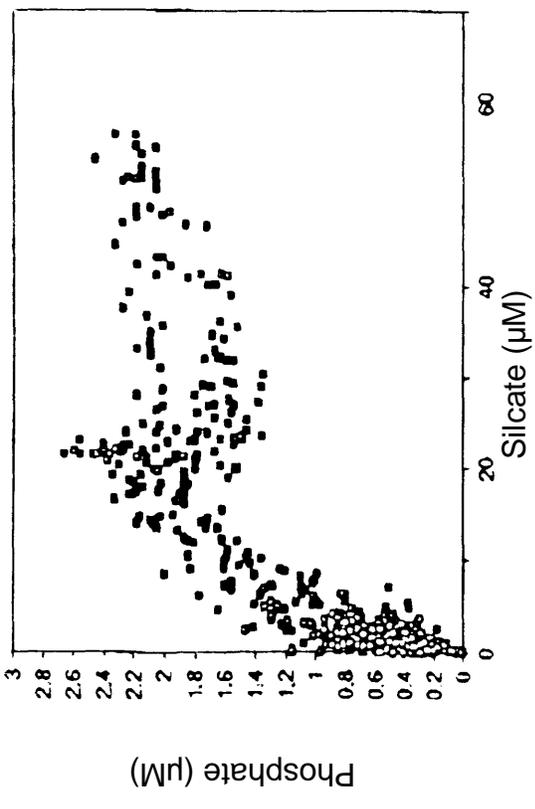
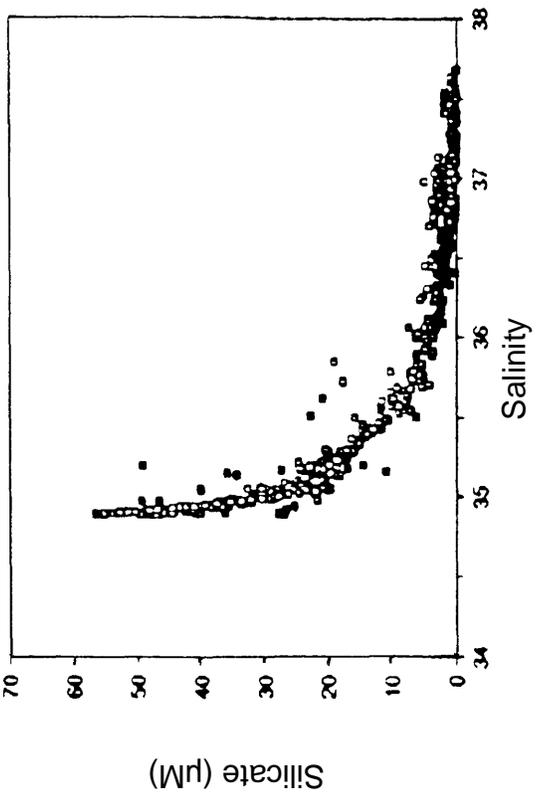
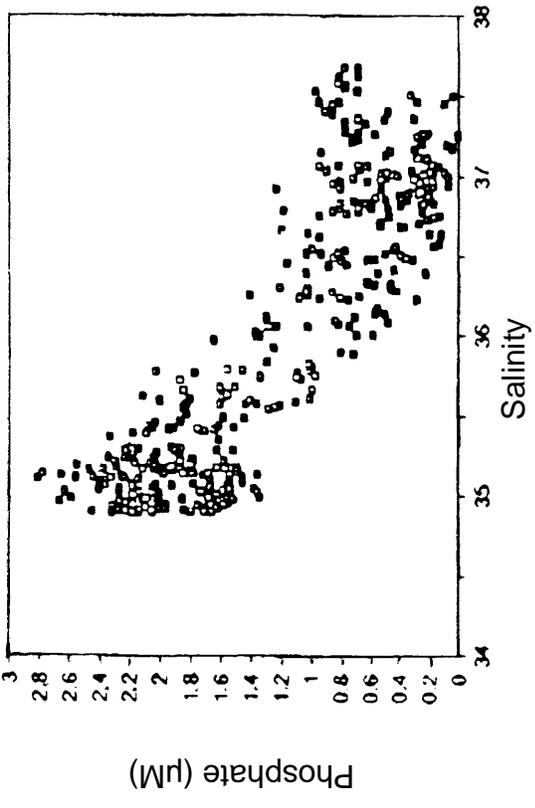


Figure 13: Nutrients diagrams.

### ***Addendum to the Nutrients Report on A05***

(A. Cruzado)

During the HE06 cruise (July/August 1992) along the WOCE line A-5, dissolved inorganic nutrients (orthophosphate, nitrate+nitrite, nitrite, and orthosilicate) were collected and analysed on board the R/V Hesperides using a continuous flow analyzer by Antonio Cruzado (Centro de Estudios Avanzados de Blanes, Spain) following methods adapted from Withledge et al. (1981). These methods were used in the fifth 1989/1990 ICES international inter-comparison exercise for nutrients in seawater (Aminot and Kirkwood, 1995). Three different quality control procedures were applied to the A5 nutrient data. First, spurious chemical data were flagged according to WOCE quality control codes. These are data values shown to be analytically incorrect ("Bad"). Second, the A5 chemical data were compared to the August 1992, Trident cruise on the RV Baldrige between Abaco Island, the Bermuda Rise and the Mid-Atlantic Ridge (Garcia, 1996). This provided a mean to compare the two cruises in the western basin only. Third, the A5 data were compared to historical oceanographic data collected since the GEOSECS program (Table 1). The long-term precision of the A5 chemical data was estimated following the method of Saunders (1986). Potential temperature (Fofonoff and Millard, 1983) was fitted to the nutrient data from the HE06 and AT109 cruises by linear least-squares for water with temperatures less than or equal to 1.8°C and 2.1°C in the western (45-75 W) and eastern (20-44 W) Atlantic basins, respectively (Garcia, 1996). The standard deviation of the measured values for each chemical variable from the expected values calculated from the coefficients of the regression lines for stations in the western and eastern basins are shown in Table 2. Chemical data points which deviated significantly (more than 5 SD from the mean) were flagged as questionable. No quality control was applied to the nitrite data.

**Table 1** Historical data (1972-92) used in this work

<b>Cruise/Leg</b>	<b>Ship</b>	<b>Cruise dates</b>	<b>Institution</b>
AT109-II	Atlantis II	August-September, 1981	WHOI
AT109-I	Atlantis II	June-July, 1981	WHOI
Trident	Baldrige	August, 1992	LDEO
EN129	Endeavor	April, 1985	WHOI
GEOSECS	Knorr	July, 1972-April, 1973	SIO
TTO-NAS	Knorr	April-October, 1981	SIO
TTO-TAS	Knorr	December-February, 1983	SIO
KN104	Knorr	July-August, 1983	WHOI
OC133-II	Oceanus	January, 1983	WHOI
OC202	Oceanus	July-September, 1988	SIO

**Table 2:** Estimates of precision (1 SD) of the AT109-II and HE06 chemical data. Numbers in parenthesis indicate the number of data points in the calculation described in the text above (Garcia, 1996).

<b>Cruise</b>	<b>Phosphate</b>	<b>N+N</b>	<b>Silicate</b>	<b>Oxygen</b>
<b>Western Atlantic (75-45 W)</b>				
AT109-II	0.04 (81)	0.5 (83)	1.8 (83)	2.2 (86)
HE06	0.08 (58)	0.3 (79)	1.9 (82)	1.4 (83)
<b>Eastern Atlantic (20-44 W)</b>				
AT109-II	0.03 (65)	0.2 (64)	0.6 (64)	1.9 (74)
HE06	0.08 (62)	0.2 (88)	0.9 (94)	1.6 (99)

### 3.5. CFC-11 and CFC-12 (W. Smethie)

The objective of the CFC measurement program on this cruise was to measure the distribution of CFC-11 and CFC-12 in the thermocline along 24°N in the Atlantic and in recently ventilated components of North Atlantic Deep Water, including the Deep Western Boundary Current, spreading southward in the western North Atlantic.

The CFC measurements were made on board with a CFC analysis system interfaced to a gas chromatograph with an electron capture detector. This method is described in Smethie et al. (1988) and is similar to the Bullister and Weiss (1988) technique.

One difference for this cruise was the use of a Porasil B precolumn and a SP21000 main column instead of Porasil B for both columns. This combination allowed CFC-113 and carbon tetrachloride to be detected as well as CFC-11 and CFC-12. However carbon tetrachloride and CFC-113 were not measured on every station because of the longer analysis time required. The purpose of these measurements was to obtain preliminary information on the distribution of these substances in the ocean and they are not of the same quality as the CFC-11 and CFC-12 measurements.

Some problems were encountered. A set of new syringes had a low level CFC-11 contamination (0.02 – 0.04 pmol/kg). Blanks for these syringes were determined and monitored by analyzing zero CFC water from the deep eastern basin or by comparison to duplicate samples collected in old syringes which were not contaminated. These blanks decreased during the cruise. There was a high (20-30% of surface water concentration) and variable CFC-113 system blank and the Niskin bottles became severely contaminated with CFC-113 at station 75, probably due to a fire control exercise by ship's personnel, and remained contaminated for the remainder of the cruise.

The general sampling strategy was to sample every other station which resulted in approximately 60 nm spacing. Every station was sampled near the western boundary. Generally 10 or 11 samples were taken between the surface and 1000 m along the entire section. In the eastern basin the deep water contained no CFCs, but samples were collected to determine Niskin bottle/sampling blanks and syringe blanks. In the western basin, CFCs were detected throughout the water column. Vertical spacing varied between 150 and 400 m with more closely spaced samples at about 1500 m and 3500-4000m to resolve CFC maxima at these levels. A section was also taken across Florida Strait with approximately 5 nm horizontal resolution and 50-100 m vertical resolution. A total of about 1100 water samples, not including duplicates, were analyzed.

In the [figure 14](#), shown are vertical profiles of preliminary shipboard values of F-11.

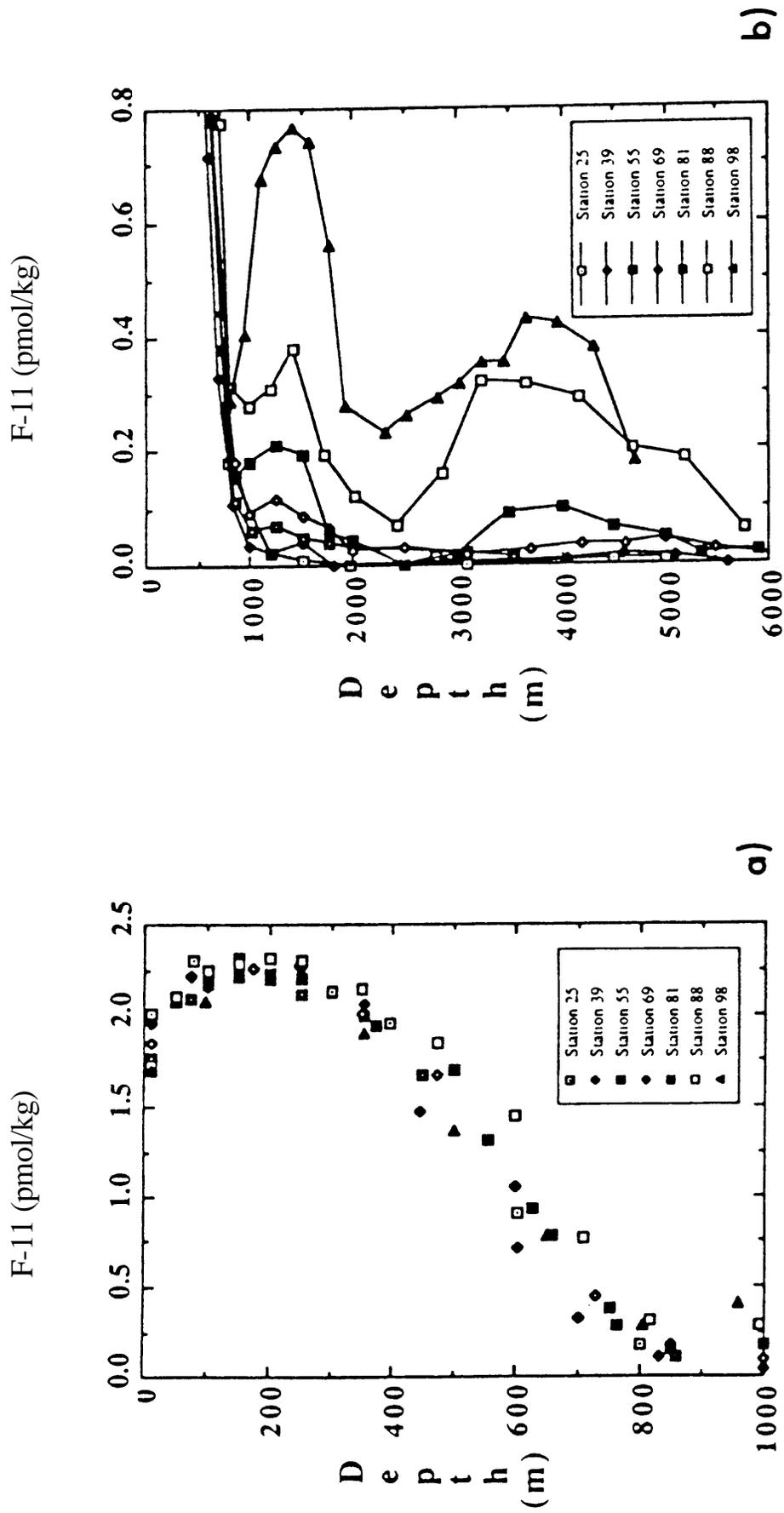


Figure 14: Vertical profiles of preliminary F-11 values at depths less than (a) and greater than (b) 1000m.

### **3.6. Particulate Organic Matter** (A.F. Ríos)

Two liters of seawater at levels (10, 15, 50, 100, 200 and 400 m) on 25 stations were filtered through a glass fiber filter (Whatman GF/F of 25 mm diameter) in order to determine the particulate carbon and nitrogen using a 2400 Perkin Elmer Elemental Analyzer.

To determine particulate phosphorous, samples of one liter of seawater retained I filters (Millipore AAWPO2500) were taken at the same stations and levels as before. These samples will be oxydized with percloric-sulphuric acid (Ríos and Fraga, 1987) and later determination of phosphate will be carried out by the method described by Grasshoff et al. (1983).

Carbohydrates will be determined by the technique of Antron reagent (Rios, 1992) from samples of one liter of seawater retained in filters (Millipore AAWP02500) taken at these same stations and levels.

**3.7. Calcium**  
(G. Rosón)

The 450 samples analyzed for this parameter were taken on 20 stations at all levels.

The method used for determining calcium is a volumetric titration of about 130 g of seawater with potentiometric detection of end point by calcium selective electrode, using EGTA (ethyleneglycol-bis) (B-aminoethyleter), N, N, N1, N1, tetraacetic acid) as titrant (0.18 M) and 25 ml of borax (0.1 M) as buffer (Rosón and Pérez, 1990; Rosón, 1992). The reproducibility of the method, made on a 25 l storage bottle, was 0.07% for 70 samples.

**3.8. Carbon-14**  
(W. Smethie for W. Broecker)

Carbon-14 samples were collected in the thermocline at a few select stations. These samples will be analyzed by accelerator mass spectrometry. This is part of a larger program to collect samples over the entire North Atlantic from ships of opportunity during the next few years. The objective is to determine the distribution of bomb carbon-14 in the thermocline and compare this distribution to the distributions measured in 1981 on the TTO program and 1972 on the GEOSECS program. The evolving bomb carbon-14 distribution will be used to investigate circulation and mixing in the thermocline and uptake of carbon dioxide by the ocean.

Samples were collected at stations 13, 24, 35, 53, 66, 81, and 92. In general 8 samples were collected at each station, one in the surface mixed layer and seven at the following sigma-theta surfaces: 26.2, 26.4, 26.6, 26.8, 27.0, 27.2, and 27.4. Samples were also collected at stations 103 (one in the oxygen maximum) and 107 (six throughout the water column) in the Straits of Florida and at test station (ten samples) just west of the Strait of Gibraltar. A total of 71 samples were collected.

**3.9. ADCP**  
(M. Garcia)

The ADCP model used was a RD-VMO 150. The selected sampling intervals were 180 s, 40 depth bins of 8 m length. The profiler was recording continuously during the whole cruise and the data was recorded on diskettes.

**3.10. Thermosalinograph**  
(E. Álvarez)

During W.O.C.E. A-5 section, temperature and salinity were measured across the Atlantic Ocean surface using a Seabird thermosalinometer (serial number 626a). Data acquisition began on station number one and finished close to Miami harbor. The time step between each acquisition was three minutes. The obtained data were stored in groups of files, each group corresponding to one navigation day. Water conductivity was recorded from the third navigation day on. Two electricity failures (during the second and fourth days) and at least one water flux stoppage (during the fourth day) interrupted the continuous time series.

**3.11. Chlorophyll Pigments and Primary Production**

Two kinds of analysis have been undertaken for pigment studies. One was based on spectrophotometric equations with readings of absorbances at 664, 645, 630 and 750 nm. In the other smaller volumes of seawater were used for analysis of chlorophyll and phaeopigments based on fluorescence readings before and after acidification of the sample.

### 3.11.1. Chlorophyll Pigments (Z.R. Velásquez)

Water samples were taken at several depths (0-250m) on all stations of the WOCE A-5 section from NW Africa to the Bahamas.

The phytoplanktonic pigments were determined on board immediately after sampling by the spectrophotometric technique described by Jeffrey and Humphrey (1975). About 3.3 liters of seawater were filtered under vacuum through 4.7 cm Whatman GF/F filters. After extraction during a minimum of 24 hours with 5 ml (90%) acetone in the dark at 0°C, the resulting suspension was centrifuged at 3000 rpm for 30 minutes.

The absorbances at 664, 645 and 630 nm, required for the computation of the concentrations of Chlorophyll A, B and C, were determined in the supernatant (5 ml), allowance being made for the eventual presence of turbidity by measuring also the absorbance at 750 nm. All absorbance measurements were done with a LBK spectrophotometer linked to a computer.

The following formula was used for the computation of the pigment concentration in the supernatant in µg/l.

(Chlorophyll (µg/l) = OD \* Vac / Vsw

$$\begin{array}{ll} \text{OD (a) = } & 11.85*(D664-D750)-1.54* & (D645-D750)-0.08*(D630-D750) \\ \text{OD (b) = } & 21.03*(D645-D750)-5.43* & (D664-D750)-2.26*(D630-D750) \\ \text{OD (c) = } & 24.52*(D645-D750)-1.67* & (D664-D750)-7.66*(D645-D750) \end{array}$$

where

$$\begin{array}{ll} \text{Vac = } & \text{volume of acetone (in ml);} \\ \text{Vsw = } & \text{volume of seawater (in l);} \\ \text{Dxxx = } & \text{optical density at wavelength xxx and 1 cm optical path} \end{array}$$

Pheopigments were determined by acidifying the extracts with two drops of 10% HCl and reading at the same wavelengths.

Samples of water at the same level were preserved with Lugol (Potassium Iodate/Iodine solution buffered with sodium acetate) for further phytoplankton analysis with an Olympus inverted microscope to which a computer/video digitizing system has been adapted.

In the [figure 17](#) vertical profiles of total chlorophyll for stations 1 through 60 are shown.

### 3.11.2. Chlorophyll Pigments and Primary Production (J. García-Braun)

Water samples were taken for pigment analysis at several depths (mainly, 0 - 200 m) on 90 stations for a total of 1152 analyses for chlorophyll and phaeophytin.

With respect to the pigment distribution in the water column, our main objectives were: to obtain the vertical distribution of chlorophyll a, based on fluorescence readings, calibrated against spectrophotometer following SCOR-UNESCO (1966) and the vertical distribution of chlorophyll and phaeophytin, based on fluorescence readings, before and after acidification, according to equations by Lorenzen (1966); and to estimate the pigments biomass including size classes, evaluating picoplankton less than 2 microns and populations bigger than 2 microns.

Two samples of 1 liter sea water for each depth were filtered through Whatman GF/F filters. Pigments were extracted in 10 ml of 90% acetone during about 12 hours in the dark at 0°C. The fluorescence measurements (before and after acidification with two drops of 10% CIH) were used to calculate the pigments according with the following equations:

$$\text{Chlorophyll a} = 11.64 e_{663} - 2.16 e_{645} + 10 e_{630}$$

where  $e_{663}$ ,  $e_{645}$  and  $e_{630}$  are the absorbances at 663, 645 and 630 nm after substraction of the absorbance at 750 nm, using 1 cm spectrophotometer cell. If the obtained value is multiplied by the extract volume in ml and divided by the volume of seawater filtered in liters, the amount of chlorophyll a in mg/m<sup>3</sup> is obtained.

The equation proposed by SCOR-UNESCO (1966) was used to calibrate the Fluorometer Turner Design in which all the readings of Fluorescence were made during the cruise. Concentrations of chlorophyll a and phaeophytin a were also calculated following the equations given by Lorenzen (1966).

Vertical profiles of chlorophyll and phaeophytin for several stations are shown in [figure 18](#).

### **3.11.3. Primary Production** (J. García-Braun)

Water samples for primary production experiments were taken at several depths in the photic zone, representing approximately 100%, 25%, 10% and 1% of surface light. The standard C14 method proposed by Steeman Nielsen (1952) was used with some modifications. The incubations were done in incubators under artificial light during 2-3 hours. The selected stations (11 stations and 99 samples) were chosen in order to make the incubations in early hours during the morning.

For each depth, samples of 100 cc of seawater were inoculated with 4  $\mu$  Ci of C14 bicarbonate. After incubation one sample was passed through Nucleopore filter (2 micron pore size) and the other sample through Whatman GF/F filters. A separate sample was incubated in the dark in order to substract the incorporated radioactivity with respect to the light bottles. The filters were preserved in the deep freeze for future readings of counts per minute in a Liquid Scintillation Counter.

### **3.12 Aluminum** (M.D. Gelado and J.J. Hernández)

A voltametric method was used for aluminum determination during WOCE-AS Cruise.

The procedure is based on complexation of aluminum with 1,2-dihydroxyanthraquinone-3-sulphonic acid (DASA) and measurement of reduction current of this complex using high speed cathodic stripping voltametry (HSCSV). Reduced Al-DASA complex produces an intensity of faradaic current proportional to dissolved Al concentration. The free DASA ligand has a cathodic peak at - 0.63 V while Al-DASA peak is more negative at -1.1 V (Ag/ClAg).

Optimal experimental parameters include an accumulation potential of -0.95 V during 45 s, DASA concentration  $2 \times 10^{-6}$  M and staircase scan mode to 30 V/s speed. Samples are buffered at 7.1 pH using N, N1bis(2-hydroxyethyl)-2-aminoethane sulphonic acid(BES). The method (Gelado-Caballero, 1992) is specially adapted for on board determinations.

The electrochemical system has been designed to measure the instantaneous currents at short times with a low noise level (Hernandez-Brito et al., 1990). Thus, the analytical time required for each sample is substantially reduced, allowing an increase of the number of measurements in situ. A PAR303A electrochemical cell with hanging mercury drop electrode (HMDE) was connected to a specially made computer-controlled potentiostat.

The detection limit was 1.75 nM for 30 s adsorption time. The deviation was less than 3% for a 19 nM Al concentration based on repetitions for 7 seawater samples.

In total 1000 samples were taken in 52 stations. In most of the stations, except in those close to the African coast, maximum was detected at the surface layers. Below a minimum at intermediate depths the dissolved Al concentrations increased with depth.

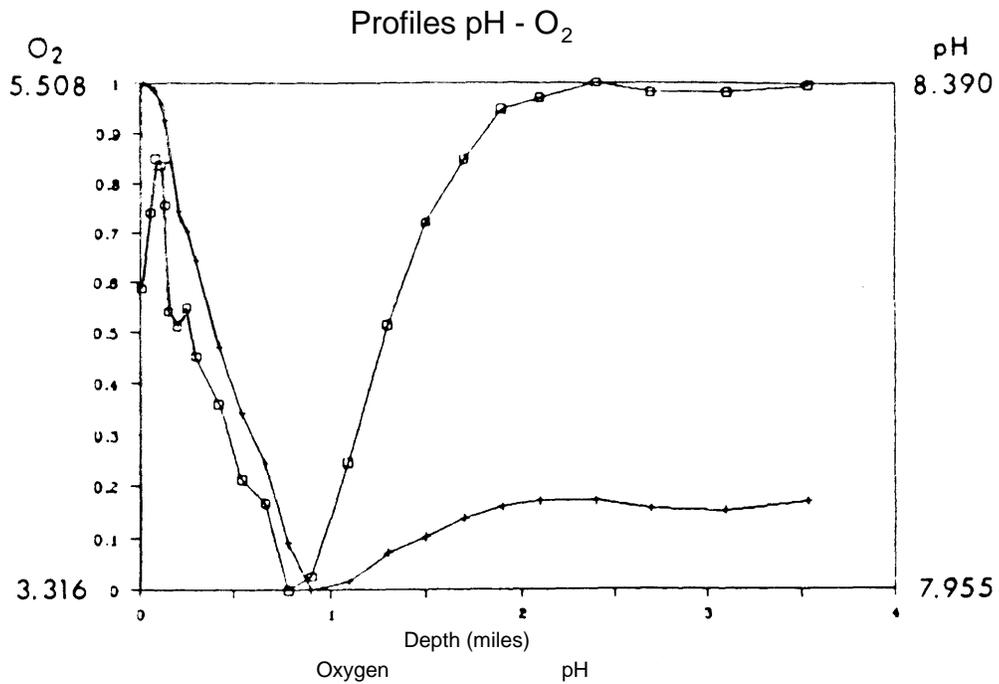


Figure 15: Vertical distribution of pH and dissolved Oxygen for station 47.

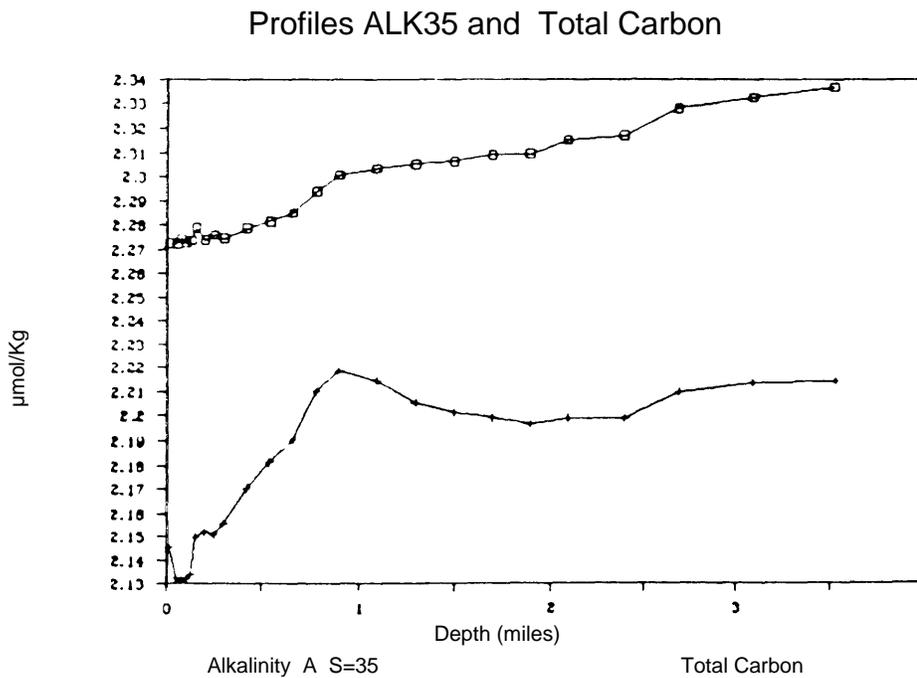


Figure 16: Vertical distribution of the alkalinity and total carbon for station 47.

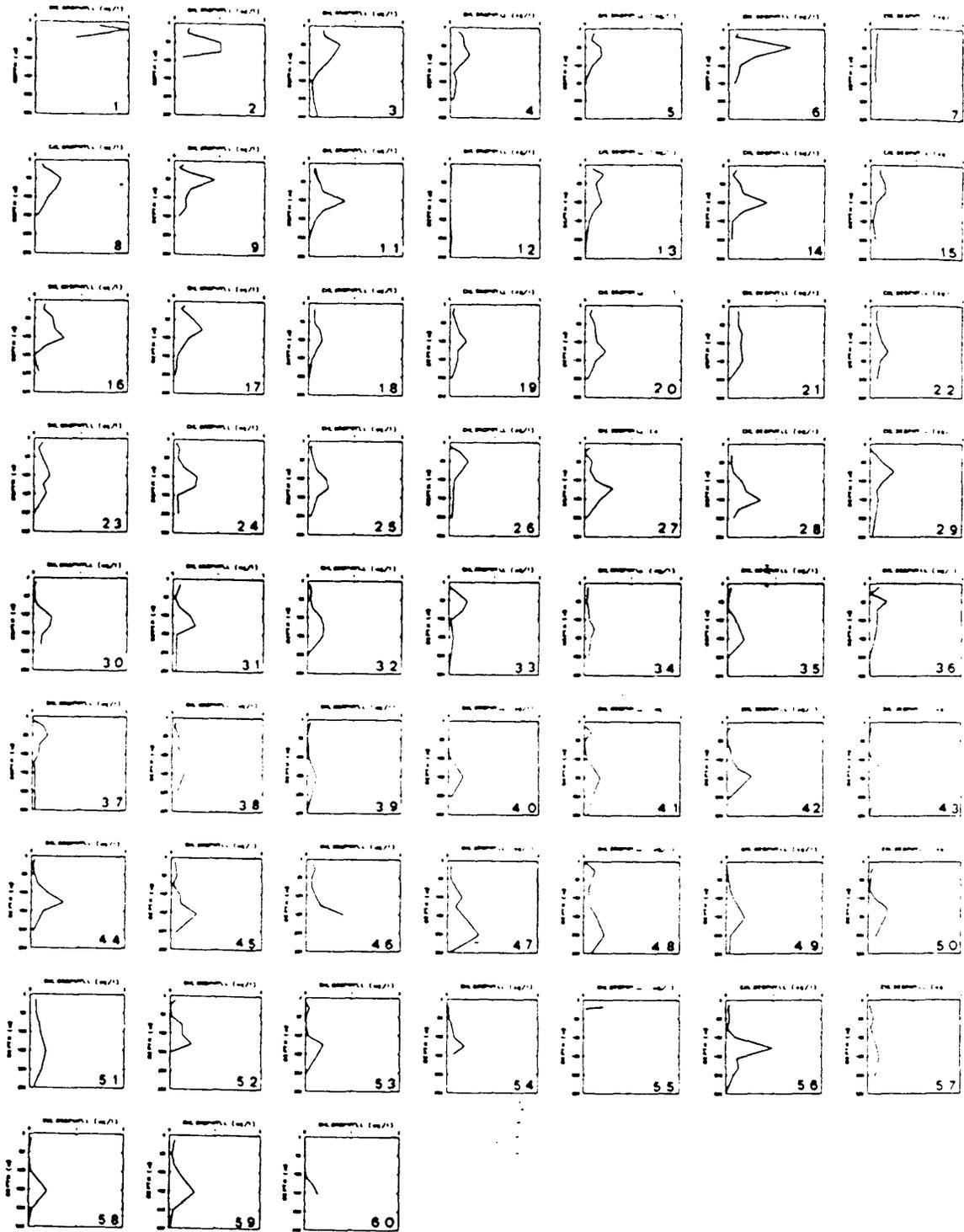


Figure 17: Vertical distribution of the chlorophyll for stations 1 to the 60.

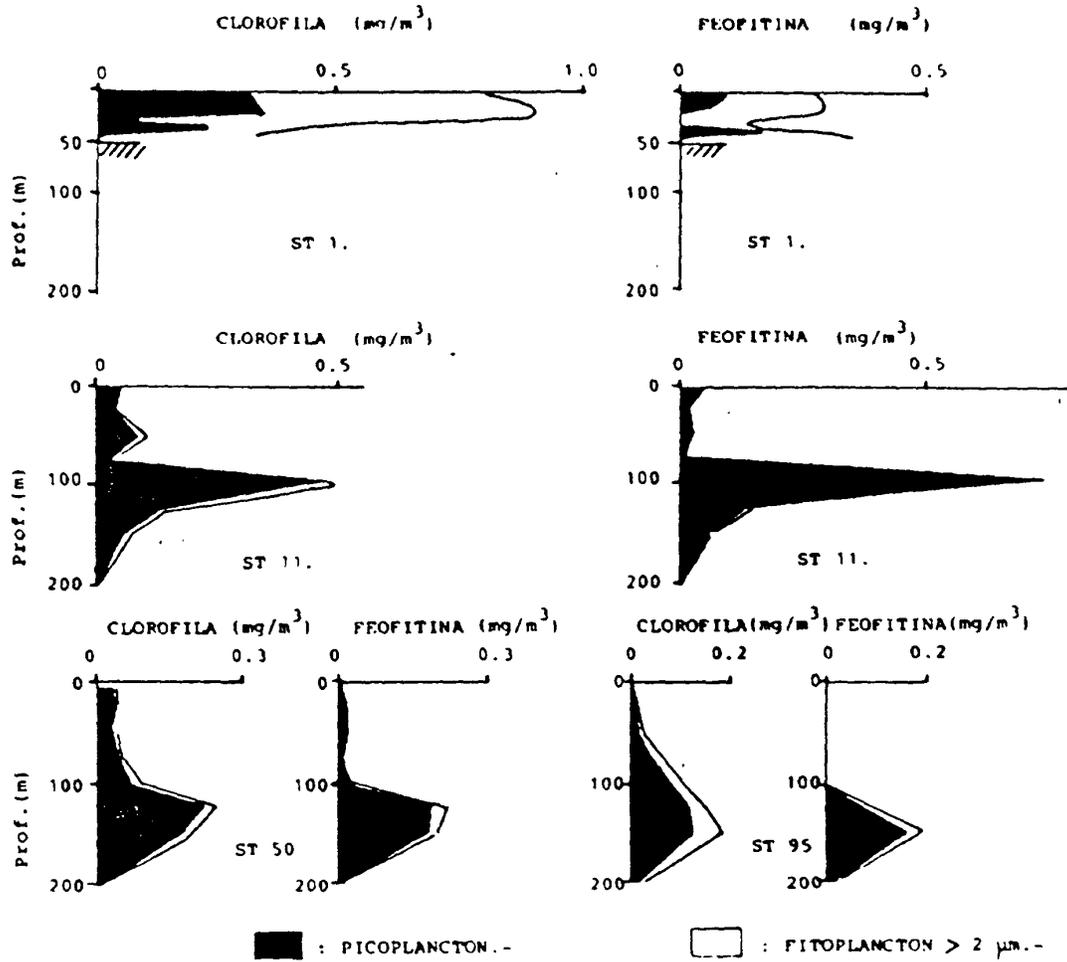


Figure 18: Vertical profiles of chlorophyll and phaeophytin for stations 1, 11, 50 and 95.

## Acknowledgements

This project was supported by IEO (Proy.1308), CICYT (Acc. Esp. AMB92-1114-E). Participation on this cruise by H. Bryden, R. Millard and G. Bond and subsequent processing and analysis of the measurements by H. Bryden and R. Millard were supported by NSF and NOAA. We are grateful to Junta de Gestión del B.I.O. Hespérides for its support and collaboration, as well as to those colleagues of the IEO who encouraged us and lent us their help. We also wish to acknowledge the seamanship, ability and friendship displayed by the captain and crew of the B.I.O. Hespérides who contributed specially to the completion of the cruise.

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Station	Pressure	Remarks
13	2025 db	SALNTY (35.050) is high compared with 35.039 upcast and 35.041 downcast CTDSAL, flag 4.
	2533 db	SALNTY (34.989) is high compared with 34.982 upcast and 34.979 downcast CTDSAL, flag 4.
	3053 db	SALNTY (34.946) is high compared with 34.940 upcast and 34.941 downcast CTDSAL, flag 3.
	4078 db	SALNTY (34.894) is low compared with 34.896 upcast and 34.896 downcast CTDSAL, flag 3, these are very deep waters.
14	SALNTYs are lower than upcast CTDSAL by at least 0.01 for the whole station, better for downcast CTDSAL. The flag is 3 for the whole station SALNTYs	
	403 db	SALNTY (35.789) is high compared with 35.742 upcast and 35.734 downcast CTDSAL, flag 4.
	4070 db	SALNTY (34.884) is low compared with 34.898 upcast and 34.899 downcast CTDSAL, flag 4.
	4377 db	SALNTY (34.881) is low compared with 34.894 upcast and 34.894 downcast CTDSAL, flag 4.
15	65 db	There is a strange 20 m thick layer of low salinity water. It is temperature compensated and even the oxygen is slightly less. It seems true because it is supported by bottle measurements although there are differences between CTDSAL and SALNTY. They can be explained by high salinity gradient. There is no such a layer on neighboring stations. I cannot make out where this freshened water could appear from in the middle of the Canary Basin.
	1515 db	There are differences between SALNTY (35.170) and downcast CTDSAL (35.157). Upcast CTDSAL matches well with SALNTY (35.172). I don't flag anything questionable and attribute these differences to tidal internal waves which are extremely large here.
	4646 db	SALNTY (34.901) is high compared with upcast 34.892 and downcast CTDSAL 34.892 flag 4.
16	762 db	SALNTY (35.223) is high compared with upcast CTDSAL 35.212 and downcast CTDSAL 35.198, flag 4.
	4734 db	SALNTY (34.905) is high compared with upcast CTDSAL 34.890 and downcast CTDSAL 34.890, flag 4.
	CTDOXY downcast calibration is wrong below 1500 db. The values are higher than OXYGEN and measurements on neighboring stations.	
	4734 db	OXYGEN (5.59) is low compared with upcast CTDOXY 5.79 and downcast CTDOXY 5.78, flag 4.
18	1316 db	SALNTY (35.158) is very low compared with upcast CTDSAL 35.220 and downcast CTDSAL 35.216, flag 4.
19	3553 db	OXYGEN (5.68) is high compared with upcast CTDOXY 5.61 and downcast CTDOXY 5.60, flag 3.
	4066 db	SALNTY (34.896) is low compared with upcast CTDSAL 34.899 and downcast CTDSAL 34.900, flag 4.
21	204 db	SALNTY (36.663) does not match with upcast CTDSAL (36.645) I flag them both 3 - Qble. There is a large salinity gradient at this pressure, but nevertheless the discrepancy is very large and they both differ from downcast CTDSAL (36.507).
22	4069 db	SALNTY (34.891) is low compared with upcast CTDSAL 34.901 and downcast CTDSAL 34.902, flag 4.

Station	Pressure	Remarks
24		You have a wonderful Meddy around 1200 db and CTDSAL is questioned by originators. It is absolutely true.
	1517 db	SALNTY (35.120) is high compared with upcast CTDSAL 35.118 and downcast CTDSAL 35.117, I don't flag these differences as questionable they must be accounted for internal waves.
	5663 db	OXYGEN (5.61) is low compared with upcast CTDOXY (5.68) and downcast CTDOXY (5.68), flag 4.
25	3107 db	OXYGEN (5.70) is high compared with upcast CTDOXY (5.65) and downcast CTDOXY (5.65), flag 3.
27	5472 db	SALNTY (34.890) is high compared with upcast CTDSAL (34.887) and downcast CTDSAL (34.888), I flag SALNTY 3.
28	2526 db	SALNTY (35.056) is high compared with upcast CTDSAL (34.985) and downcast CTDSAL (34.991). Originators flag upcast CTDSAL Qble, I flag SALNTY 4.
	4067 db	SALNTY (34.908) is high compared with upcast CTDSAL (34.900) and downcast CTDSAL (34.902), I flag SALNTY 4.
	4581 db	SALNTY (34.894) is high compared with upcast CTDSAL (34.891) and downcast CTDSAL (34.892), I flag SALNTY 3.
	5092 db	SALNTY (34.890) is high compared with upcast CTDSAL (34.886) and downcast CTDSAL (34.888), I flag SALNTY 3.
28	5718 db	SALNTY (34.888) is high compared with upcast CTDSAL (34.886) and downcast CTDSAL (34.886), I flag SALNTY 3.
29	1213 db	OXYGEN (4.36) is high compared with upcast CTDOXY (4.15) and downcast CTDOXY (4.12), flag 4.
	2430 db	OXYGEN (5.48) is low compared with upcast CTDOXY (5.58) and downcast CTDOXY (5.58), flag 4.
30	5613 db	SALNTY (34.887) is high compared with upcast CTDSAL (34.884) and downcast CTDSAL (34.885), I flag SALNTY 3.
	5924 db	SALNTY (34.886) is high compared with upcast CTDSAL (34.884) and downcast CTDSAL (34.884), I flag SALNTY 3.
31	1517 db	SALNTY (35.165) is high compared with upcast CTDSAL (35.163) and downcast CTDSAL (35.154), I do not flag these data questionable as I think that the differences are caused by internal waves.
30 - 32		Calibration of downcast CTDOXY is wrong in the interval 2000-5500. CTDOXY is lower than bottle measurements
33	809 db	OXYGEN (3.65) is high compared with upcast CTDOXY(3.42) and downcast CTDOXY (3.35), flag - 4.
34	3556 db	OXYGEN (5.73) is high compared with upcast CTDOXY (5.62) and downcast CTDOXY (5.61), flag 4.
	4066 db	OXYGEN (5.72) is high compared with upcast CTDOXY (5.66) and downcast CTDOXY (5.65), flag 4.
	4572 db	SALNTY (34.898) is high compared with upcast CTDSAL (34.891) and downcast CTDSAL (34.892), I flag SALNTY 4.
	5091 db	SALNTY (34.879) is low compared with upcast CTDSAL (34.884) and downcast CTDSAL (34.885), I flag SALNTY 4.
35	3555 db	SALNTY (34.912) is low compared with upcast CTDSAL (34.914) and downcast CTDSAL (34.916), I flag SALNTY 3.
	4068 db	SALNTY (34.895) is low compared with upcast CTDSAL (34.899) and downcast CTDSAL (34.899), I flag SALNTY 4.
	4581 db	SALNTY (34.888) is low compared with upcast CTDSAL (34.892) and downcast CTDSAL (34.893), I flag SALNTY 4.

Station	Pressure	Remarks
35, 36		Calibration of downcast CTDOXY is wrong in the interval 2500-4500. CTDOXY is lower than bottle measurements and measurements on neighboring stations.
37	4068 db	SALNTY (34.902) is low compared with upcast CTDSAL (34.903) and downcast CTDSAL (34.905), I flag SALNTY 3.
38	3001 db	SALNTY (34.973) is high compared with upcast CTDSAL (34.945) and downcast CTDSAL (34.945), I flag SALNTY 4.
37, 38		Calibration of downcast CTDOXY is wrong in the interval below 1500 db. CTDOXY is higher than bottle measurements and measurements on neighboring stations.
40		Calibration of downcast CTDOXY is wrong in the interval 1800-2800. CTDOXY is higher than bottle measurements and measurements on neighboring stations.
44	4998 db	SALNTY (34.887) is low compared with upcast CTDSAL (34.889) and downcast CTDSAL (34.890), I flag SALNTY 3.
46	4434 db	SALNTY (34.903) is high compared with upcast CTDSAL (34.900) and downcast CTDSAL (34.900), I flag SALNTY 3.

#### Western part

Salinity and oxygen are examined separately because there were many problems with CTDOXY calibration.

#### Salinity

Station	Pressure	Remarks
58	2535 db	SALNTY (34.980) is high compared with upcast CTDSAL (34.960) and downcast CTDSAL (34.962), I flag SALNTY 4.
64		Some bad CTDSAL measurements are flagged 3 -Qble. They are really bad.
67	5012 db	SALNTY (34.846) is low compared with upcast CTDSAL (34.855) and downcast CTDSAL (34.855), I flag SALNTY 4.
75	4579 db	SALNTY (34.886) is low compared with upcast CTDSAL (34.889) and downcast CTDSAL (34.890), I flag SALNTY 3.
	5609 db	SALNTY (34.842) is low compared with upcast CTDSAL (34.844) and downcast CTDSAL (34.845), I flag SALNTY 3.
83	1703 db	SALNTY (35.000) is low compared with upcast CTDSAL (35.030) and downcast CTDSAL (35.030), I flag SALNTY 4.
89		There is great difference between SALNTY and upcast and downcast CTDSAL in the upper 80 db layer. Bottle samples taken at 11; 28; 53; 77 dbars

## Oxygen

There are problems with calibration of CTD oxygen sensor for many of the stations. Some CTD casts contain data that are definitely bad and they are not flagged bad at all.

Station	Pressure	Remarks
52	2002 db	OXYGEN (5.65) is high compared with upcast CTDOXY (5.60) and downcast CTDOXY (5.57), flag - 4.
53	1518 db	OXYGEN (5.27) is high compared with upcast CTDOXY (5.14) and downcast CTDOXY (5.14), flag - 4.
55	3973 db	OXYGEN (5.84) is low compared with upcast CTDOXY (5.87) and downcast CTDOXY (5.88), flag - 4.
58	5157 db	OXYGEN (5.75) is low compared with upcast CTDOXY (5.80) and downcast CTDOXY (5.82), flag - 4.
63	4306 db	OXYGEN (5.85) is high compared with upcast CTDOXY (5.79) and downcast CTDOXY (5.80), flag - 4.
68	3564 db	OXYGEN (5.96) is high compared with upcast CTDOXY (5.87) and downcast CTDOXY (5.87), flag - 4. CTDOXY calibration is wrong below 2500 db. CTD measurements are less than bottle.
69		CTDOXY calibration is wrong below 5000 db. CTD measurements are less than bottle OXYGEN approximately by 0.02ml/l.
70	2505 db	OXYGEN (5.72) is low compared with upcast CTDOXY (5.80) and downcast CTDOXY (5.80), flag - 4. Almost all CTDOXY measurements to the west of station 70 are noisy. Many of them have wrong CTDOXY calibration mostly in deep waters.
73		CTDOXY calibration is wrong below 1500 db. CTD measurements are less than bottle OXYGEN approximately by 0.02ml/l.
74		CTDOXY calibration is wrong below 5000 db. CTD measurements are greater than bottle OXYGEN approximately by 0.02ml/l.
84		CTDOXY calibration is wrong below 1500 db. CTD measurements are less than bottle OXYGEN approximately by 0.02ml/l.
85		CTDOXY calibration is wrong in the interval 2500-4000 db. CTD measurements are lower than bottle OXYGEN approximately by 0.02ml/l.
86		CTDOXY calibration is wrong below 1500 db. CTD measurements are lower than bottle OXYGEN approximately by 0.02ml/l.
87		CTDOXY calibration is wrong below 1500 db. CTD measurements are lower than bottle OXYGEN approximately by 0.02ml/l.
88		CTDOXY calibration is wrong below 1500 db. CTD measurements are lower than bottle OXYGEN approximately by 0.02ml/l.
89	4003 db	OXYGEN (6.06) is high compared with upcast CTDOXY (6.17) and downcast CTDOXY (6.15), flag - 4. The calibration is better but problems below 5000 db. CTDOXY is higher than norm.
95	5408 db	OXYGEN (6.03) is high compared with upcast CTDOXY (5.97) and downcast CTDOXY (5.94), flag - 4.
97	1904 db	OXYGEN (5.80) is low compared with upcast CTDOXY (6.01) and downcast CTDOXY (5.99), flag - 4.
99		CTDOXY calibration is wrong below 2500 db. CTD measurements are lower than bottle OXYGEN approximately by 0.02ml/l.
107		618 db sample 15 OXYGEN is bad, flag - 4. 622 db sample 14 OXYGEN is bad, flag - 4.
109-111		The stations are not deep. CTDOXY calibration is bad in the entire depth.

## WHPO Data Processing Notes

Date	Contact	Data Type	Summary
1994-01-14	Smethie	CFCs	Submitted for DQE
1995-02-02	Parrilla	BTL	original data submission
1995-05-02	Parrilla	CTD/S/O	DQE Report sent to PI
1995-05-02	Morozov	CTD/S/O	DQE Report Submitted
1997-05-08	Parrilla	BTL/DOC	Submitted for DQE includes NUTs, supplement to DOC file
1997-06-08	Peng	DELC14	Submitted via email: txt/ unformatted
1997-11-21	Parrilla	SUM/SEA/CTD	Data are Public
1997-12-09	Rios	ALKALI	Submitted
1998-02-04	Kozyr	CO2	Final Data Submitted I have put 2 files with final CO2-related data to your ftp area: File a15co2fin.dat is the data obtained during the R/V Knorr cruise along WOCE Section A15. The data were submitted to CDIAC by Dr. Catherine Goyet of WHOI. File a5co2fin.dat is the data obtained during Spanish R/V Hesperides cruise along WOCE Section A5. These data were submitted to CDIAC by Dr. Frank Millero of RSMAS.
1999-04-14	Kappa	Cruise Report	PDF version made
1999-04-30	Kappa	Cruise Report	PDF Version Made a05_cruzpln.pdf added
1999-11-15	Buck	Cruise Report	Website Updated: pdf version created & online
2000-02-14	Kozyr	ALKALI/TCARBON/PH	DQE'd Data Submitted I've just put a total of 13 files [carbon data measured in Indian (6 files) and Atlantic (7 files) oceans] to the WHPO ftp area.
2000-05-22	Huynh	Cruise Report	Website Updated: files added to website
2000-05-24	Kozyr	CO2	Final Data Submitted Frank Millero has adjusted his 1992 A5 TCO2 and pH measurements right before our NDP went to press. I have changed these numbers in the data file for this cruise and put it in your INCOMING area. Please use this file when you merge the CO2 data into your hydro file.
2000-05-30	Kozyr	CO2	Final Data Submitted please replace the A5 data file I have put to your ftp site on May 24 with the a5.dat file I've put today. I found some problems in pH data. Now all data are correct and final and public.
2000-09-07	Chapman	DELC14	Submitted re-submission of Peng's 6/8/97 email w/ data
2000-10-31	Bartolacci	BTL/SUM	Website Updated: Reformatted BTL/SUM files online. OXY values converted. replaced the current online sumfile and bottle file with reformatted files produced by S. Anderson. Please note in addition to usual reformatting procedures, the oxygen values were converted from ML/L to UMOL/KG, however it is unclear and as yet unknown whether the nutrient units are correct or mislabeled.

## WHPO Data Processing Notes

<b>Date</b>	<b>Contact</b>	<b>Data Type</b>	<b>Summary</b>
2000-12-11	Uribe	Cruise Report	Submitted; found in sum file directory 2000.12.11 KJU File contained here is a CRUISE SUMMARY and NOT sumfile. Documentation is online. 2000.10.11 KJU Files were found in incoming directory under whp_reports. This directory was zipped, files were separated and placed under proper cruise. All of them are sum files. Received 1997 August 15th.
2001-03-21	Uribe	CTD	Website Updated: (Expocodes) Expocodes in all ctd files have been edited to match the underscored expocode in the sum and bottle files. New files were zipped and replaced existing ctd files online. Old files were moved to original directory.
2001-06-21	Uribe	CTD/BTL	Online CSV file modified The exchange bottle file name in directory and index file was modified to lower case. CTD exchange files were put online.
2001-11-29	Peng	DELC14	Data are Public Jim Swift called Peng to verify public status
2001-12-02	Diggs	CTD	Website Updated: Exchange file online CTD-Exchange files updated and placed online. It was a simple matter of using my new code to generate the CTD files.
2001-12-02	Diggs	C14	Re-submitted T.S. Peng's A05 C14 data from 6/7/1997 is ready and waiting to be decyphered and merged. We suffered a disk crash when these data were sent, but luckily, T.S. Peng sent a copy to Piers Chapman of TAMU and he forwarded these data on to the WHPO on 9/7/2001. T.S. Peng originally sent this file via email.
2001-12-20	Hajrasuliha	CTD	Internal DQE completed Created *check.txt file for this cruise. sal and oxy .Ps files have Not been created for this cruise.
2002-08-16	Diggs	BTL	Data merge requested Danie, Could you please merge these 14C values into the online bottle file for WOCE line A05? If you have questions, please let me know.
2002-08-20	Uribe	CTD	Flags edited, exchange files remade Original CTD files had a problem on a couple of files. Some lines were given 0 as a flag. This was changed to 9 and -9 for NUMB of OBS. Exchange/NetCDF files were remade.

## WHPO Data Processing Notes

Date	Contact	Data Type	Summary
2002-08-21	Key	BTL	Update Needed <p>The data disposition is:  Public  The bottle file has the following parameters:  STATION, CAST, BTLNBR, CTDPRS, DELC14, C14ERR, C14F  The file format is:  Comma Separated Values  The archive type is:  NONE - Individual File  The data type(s) is:  Bottle Data (hyd)  The file contains these water sample identifiers:  Cast Number (CASTNO)  Station Number(STATNO)  Bottle Number (BTLNBR)  KEY, BOB would like the following action(s) taken on the data:  Merge Data  Place Data Online  Any additional notes are:  Data Rcd by me from J. Severinghaus on 8/21/02. I think that W. Broecker should be listed as PI for these data. I assigned QC flags, but since the A20/A22 data are not yet available all existing values are flagged 2</p>
2002-08-21	Anderson	C14/CO2	C14/pH/ALK/TC02 Online Merged the DELC14 and C14ERR submitted by Bob Key. Made new exchange file. More a05 notes: Merged the DELC14 and C14ERR data submitted by Bob Key. Moved the submitted file from the website submittal area to ...a05/original/20020821.065747_KEY_A05_A05.C14. Station 108, cast 1, sample 3 had 5 identical values. The mrgsea program only merges the first one. Sarilee Anderso
2003-03-21	Kozyr	CFCs	CFCs flags are wrong Could you check a05hy.txt file (EXPCODE 29HE06_1 WHP-ID A05 DATES 072092-081792 20020821WHPOSIOSA), it has wrong CFCs flags.
2003-04-11	Anderson	CFCs	Flags corrected Corrected wrong cfc flags by remerging cfc's from a05_sea.txt found in original directory into online file. Made new exchange file, sent notes to Jerry. Alex Kozyr noted (see 2003-03-21 e-mail) that the flags for CFC11 and CFC12 were not correct. The flags were all 1s. I found a file in the a05/original directory (a05_sea.txt) that had cfc's with correct flags. I did a comparison of the cfc11 and cfc12 values between this file and the online file. The values are the same. I copied the QUALT1 flags to the QUALT2 flags for both files and then merged the cfc's from the a05_sea.txt file into the online file 2020821WHPOSIOSA.
2003-08-14	Coartney	Cruise Report	New PDF and text docs online

## WHPO Data Processing Notes

<b>Date</b>	<b>Contact</b>	<b>Data Type</b>	<b>Summary</b>
2005-01-28	Kozyr	CO2	<p>Data Report available on CDIAC website You can find the information for Indian Ocean in 2002 on Charles Darwin cruise at: <a href="http://cdiac.ornl.gov/oceans/RepeatSections/clivar_i05.html">http://cdiac.ornl.gov/oceans/RepeatSections/clivar_i05.html</a> and 26°N in the Atlantic <a href="http://cdiac.ornl.gov/oceans/RepeatSections/clivar_a05.html">http://cdiac.ornl.gov/oceans/RepeatSections/clivar_a05.html</a> However we do not have any data submitted by PIs from these cruises. Please, let me know, if you get more information or even better the data from these cruises. And if I have anything, I will let you know. I am planning to make the Repeat Section Cruise summary Table that I've sent you last week in .doc format available on line as an HTML document through our web site. I am off to the European CarboOcean Program kick off meeting next week, so I will make this table available after I come back.</p>
2005-06-16	Kozyr	CO2	<p>Submitted Final Data I have put 2 files with final CO2-related data to your ftp area: File a15co2fin.dat is the data obtained during the R/V Knorr cruise along WOCE Section A15. The data were submitted to CDIAC by Dr. Catherine Goyet of WHOI. File a5co2fin.dat is the data obtained during Spanish R/V Hesperides cruise along WOCE Section A5. These data were submitted to CDIAC by Dr. Frank Millero of RSMAS.</p>
2007-06-20	Kappa	Cruise Report	<p>Updated; CO2 Report added Incorporated Kozyr's carbon report into cruise report; updated these Data Processing Notes, re-numbered figs</p>