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Carbon Dioxide, Hydrographic, and Chemical Data Obtained During the R/V *Hespérides* Cruise in the Atlantic Ocean

(WOCE Section A5, July 14 – August 15, 1992)

Instituto Español de Oceanografía, Madrid, Spain

Carbon Dioxide Information Analysis Center
Oak Ridge National Laboratory, Oak Ridge, Tennessee

Rosenstiel School of Marine and Atmospheric Science
University of Miami, Miami, Florida

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CARBON DIOXIDE, HYDROGRAPHIC, AND CHEMICAL DATA OBTAINED DURING THE R/V *HESPÉRIDES* CRUISE IN THE ATLANTIC OCEAN (WOCE SECTION A5, JULY 14 – AUGUST 15, 1992)

Contributed by
Frank J. Millero,[1] Sara Fiol,[1] Douglas M. Campbell,[1]
and Gregorio Parrilla[2]

[1]Rosenstiel School of Marine and Atmospheric Science
University of Miami
Miami, Florida

[2]Instituto Español de Oceanografía
Madrid, 28002, Spain

Prepared by Linda J. Allison and Alexander Kozyr[3]
Carbon Dioxide Information Analysis Center
Oak Ridge National Laboratory
Oak Ridge, Tennessee

[3]Energy, Environment, and Resources Center
The University of Tennessee
Knoxville, Tennessee

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ACRONYMS

^{14}C	radiocarbon
ADCP	acoustic Doppler current profiler
ASCII	American Standard Code for Information Interchange
CDIAC	Carbon Dioxide Information Analysis Center
CEAB	El Centro de Estudios Avanzados de Blanes
CFC	chlorofluorocarbon
CO_2	carbon dioxide
CRM	certified reference material
CTD	conductivity, temperature, and depth sensor
DOE	U.S. Department of Energy
emf	electromotive force
FCMLP	Facultad de Ciencias del Mar
fCO_2	fugacity of 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	Instituto 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
R/V	research vessel
SIO	Scripps Institution of Oceanography
TALK	total alkalinity
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 A5, 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_2), total alkalinity (TALK), and pH at hydrographic stations during the R/V *Hespérides* oceanographic cruise in the Atlantic Ocean (Section A5). 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 A5 included CTD pressure, temperature, salinity, and oxygen; and bottle salinity, oxygen, phosphate, nitrate, nitrite, silicate, TCO_2, TALK, and pH.

The TALK, TCO_2, and pH were determined from titrations of seawater collected at 33 stations. The titration systems for measuring TALK and TCO_2 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 ±2 μmol/kg for TALK and ±1 μmol/kg for TCO_2. The titration systems used to measure pH were calibrated with TRIS seawater buffers prepared in the laboratory and measured with an H_2, 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 ±0.01 and are internally consistent with the measured values of TALK and TCO_2 to ±7 μmol/kg. The measured carbon dioxide system parameters have been used to calculate the in situ values of the fugacity of CO_2 (fCO_2) for the surface water. The surface results are briefly discussed.

WOCE section A5 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_2 to and from the North Atlantic.

The WOCE Section A5 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

1. BACKGROUND INFORMATION

There is currently much interest in understanding the inorganic carbon dioxide (CO_2) system in the oceans. This is due to the increasing atmospheric concentration of CO_2 enhancing the earth-atmosphere system's natural greenhouse effect and potentially affecting the earth's climate. Approximately 40% of the 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 CO_2 in the atmosphere and in the surface waters. Once the 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 ($CaCO_3$) in the oceans. The carbon dioxide system can be characterized by measuring two of the four measurable parameters [pH, the fugacity of CO_2 (fCO_2), the total carbon dioxide (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 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 TCO_2, TALK, and pH. Preferred analytical methods are coulometery for TCO_2, titration for TALK, spectroscopy for pH, and infrared (IR) or gas chromatography (GC) for fCO_2. Because coulometry and IR or GC systems to measure TCO_2 and fCO_2, respectively, were not available on the R/V *Hespérides* cruise, and because only one berth was available, the TALK, 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 A5 (along 24.5° N) (Fig. 1).

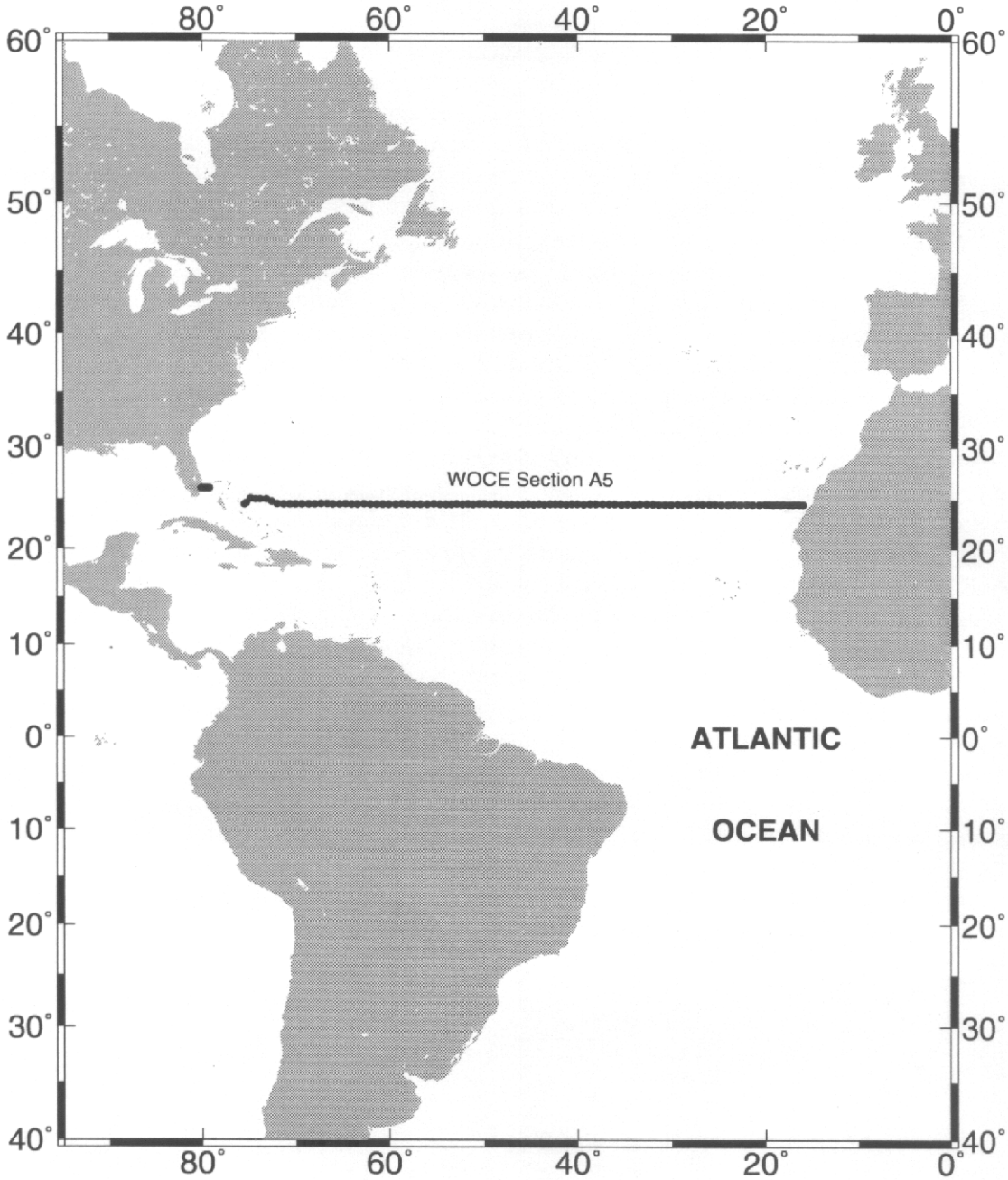

Fig. 1. The cruise track during R/V *Hespérides* Cruise HE06 (WOCE Section A5).

2. DESCRIPTION OF THE EXPEDITION

2.1 R/V *Hespérides* Cruise Information

Ship name	R/V *Hespérides*
Expedition code	29HE06/1
WOCE Section	A5
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

Parameters measured	**Institution**	**Principal Investigator**
CTD[1]	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_2	IIM	A. Rios
	RSMAS	F. Millero
Calcium	IIM	G. Roson
Chlorophyll pigments	IEO	J. García Braun
	CEAB	Z. Velazquez
Primary productivity	IEO	J. García Braun
Aluminum	FCMLP	J. Hernández
Radiocarbon (^{14}C)	LDEO	W. Broecker
ADCP[2]	UPC	M. García

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

[1]Conductivity, temperature, and depth sensor.
[2]Acoustic Doppler current profiler.

2.2 Brief Cruise Summary

According to the WOCE Implementation Plan, the cruise line for WOCE Section A5 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 A5 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 A5 the same day. After 101 stations were made, the ship arrived at the Bahamas on August 14 and WOCE Section A5 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 A5 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_2 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 ^{14}C contamination by the Tritium Laboratory of the University of Miami.

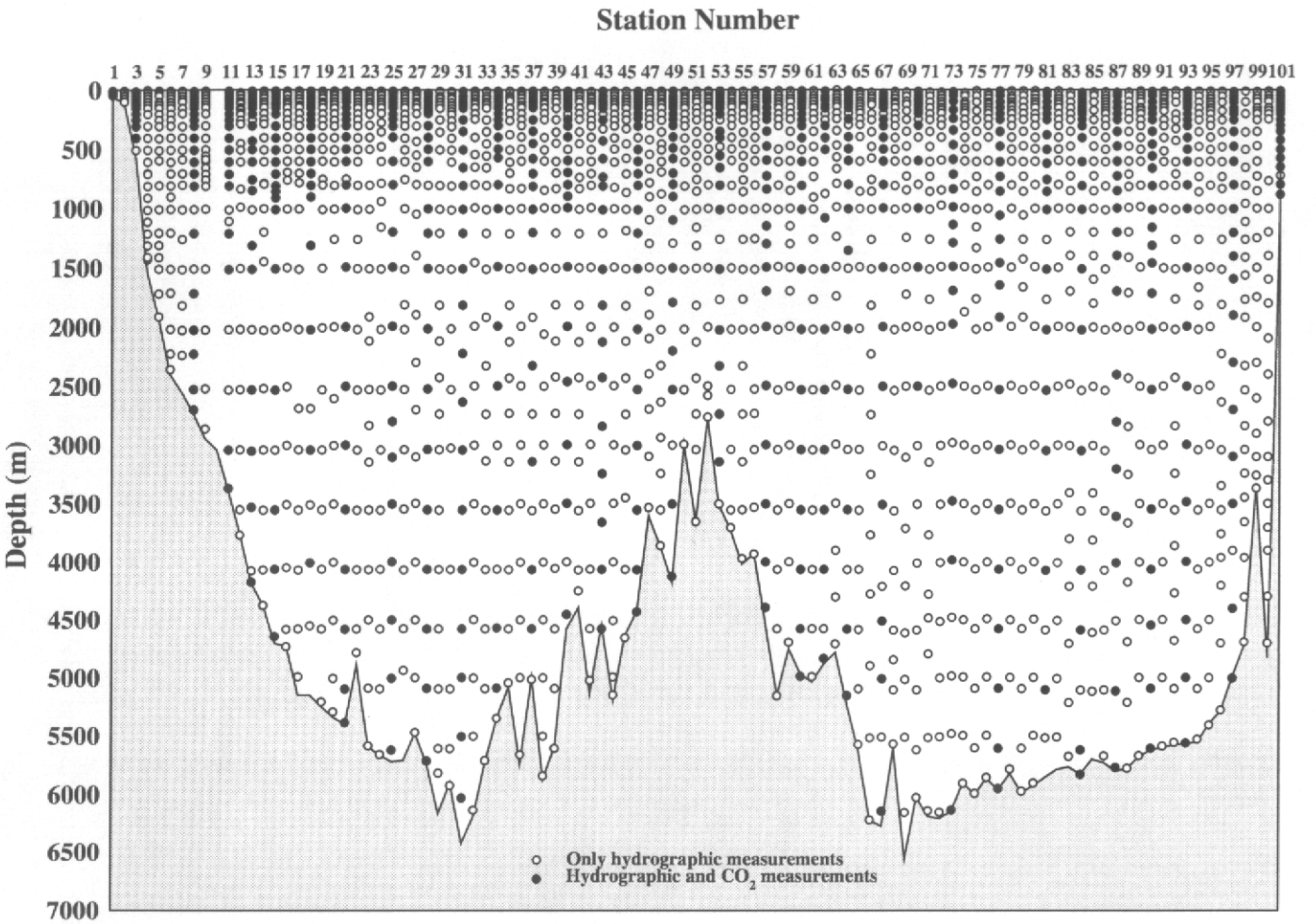

Fig. 2. Sampling depths at all hydrographic stations occupied during R/V *Hespérides* expedition along WOCE Section A5.

3. DESCRIPTION OF VARIABLES AND METHODS

3.1. 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® 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-controlled 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 tritration was determined visually using starch as the indicator. Reagents were dispensed with 0- to 2-ml capacity Dispensette® 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® 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 Whitledge 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 Whitledge 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.

3.2 Carbon Measurements

The total alkalinity (TALK), total carbon dioxide (TCO_2), 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 ±0.005.

3.2.1 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 ≈3.5). The solutions were contained in water-jacketed cells (230 cm^3) 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 BASIC 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 preassigned 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-Nerstian 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_2 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 = ≥2 and ≤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_2, and pH of TCO_2 CRMs. The results are

given in Table 2. The results indicate that precise values of TALK (±1.8 μmol/kg), TCO_2 (±5 μmol/kg), and pH (±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^3)	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_2	pH	N
Batch #12	2227.0 ± 1.8	2002.0 ± 5	7.930 ± 0.01	13
			7.942 ± 0.0005[a]	
Standard	2226.6	1984	7.940 ± 0.0002[b]	

[a]Calculated from the initial emf using TRIS buffer calibration.
[b]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^3 bottles for use at sea. The acid was standardized by titrating weighed amounts of Na_2CO_3 and TRIS dissolved in 0.7-M NaCl solution. The blanks in the 0.7-M NaCl solutions were determined by using coulometery and by titrations of the NaCl solutions with and without added Na_2CO_3 and TRIS. The TCO_2 in the blanks and carbonate solutions was measured daily by a UIC coulometer. The coulometer was calibrated using CO_2 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_2CO_3 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^3 and the values were determined to ±0.03 cm^3. 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_2 parameters (pH_{sws}, emf, TALK, TCO_2, and pK_1*) in Na_2CO_3 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_{HCl}), 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_1* is allowed to vary, and 1.5 μmol/kg when pK_1* 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).

3.2.2 Calibrations

Before the cruise, a number of titrations were made on CRMs (#12) in the laboratory. The laboratory titration results for TALK, TCO_2, and pH are given in Table 2 along with the assigned TCO_2 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):

$$\mathbf{pH_{sws} = -log[H^+]_{sws} = -log\{[H^+] + [HSO_4^-] + [HF]\}} \quad (1)$$

The precision in the values of TALK (±2 μmol/kg), TCO_2 (±5 μmol/kg), and pH (±0.005) was quite good. The titration values of TCO_2 were 18 ± 4 μmol/kg higher than the values assigned and measured by coulometery. 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_2 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_2 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_2 than for TALK. Errors of 1.0 mV in the slope yielded differences in TALK and TCO_2, respectively, of 2.1 and 22.8 μmol/kg when the pK_1^* 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_2 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_2 = 1984 μmol/kg). These calculations indicated that the deviations in the TCO_2 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_2. This fact was used to make sure that the field titration measurements yielded the most reliable values of pH and TCO_2.

During the cruise, the electrodes in each titration system were calibrated with TRIS seawater buffers (Millero 1986) of known pH_{sws} (8.057) determined with a H_2, 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_2 = 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_2, and to ±0.005 for pH (Millero et al. 1993a).

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

Cell	TALK	TCO_2	pH	N
1	2229 ± 6	1983 ± 5	7.937 ± 0.009[a]	14
6	2230 ± 8	1981 ± 8	7.944 ± 0.021[a]	5
7	2229 ± 6	1984 ± 8	7.948 ± 0.013[a]	12
Average	2229 ± 7	1984 ± 6	7.942 ± 0.014	31
Standard	2226.6[b]	1984[c]	7.940[d]	

[a]Calculated from the initial emf using TRIS buffer calibration.
[b]Certified value from weighted titrations.
[c]Certified value from manometric extraction technique.
[d]Results obtained in the laboratory using spectrophotometric methods.

3.2.3 Results

The cruise track of the R/V *Hespérides* is shown in Fig. 1. A summary of the 33 TCO_2 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_2 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_2 (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_2, 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_2 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_2 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_2 is 1970 ± 20 μmol/kg. The in situ fugacities of CO_2 (fCO_2) calculated from the measured values of TALK and TCO_2 are shown in Fig. 8. From these calculations, the surface waters ($fCO2$ = 402 ± 15 μatm) are supersaturated with CO_2 (ΔfCO_2 = 42 ± 15 μatm) for all the surface waters.

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

Station no.	Latitude (° N)	Longitude (° 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

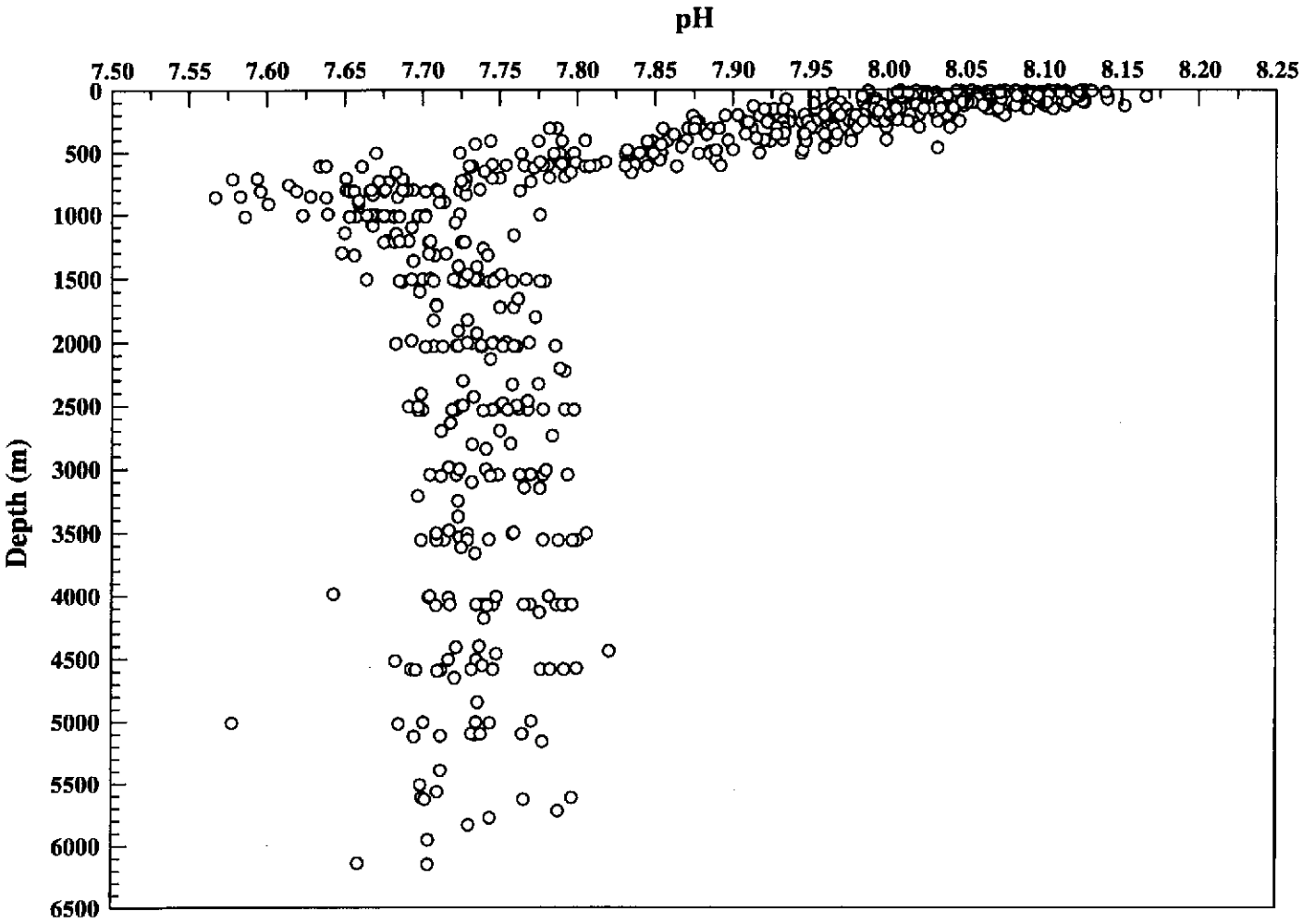

Fig. 3. Measured values of pH at 25°C vs depth for all stations.

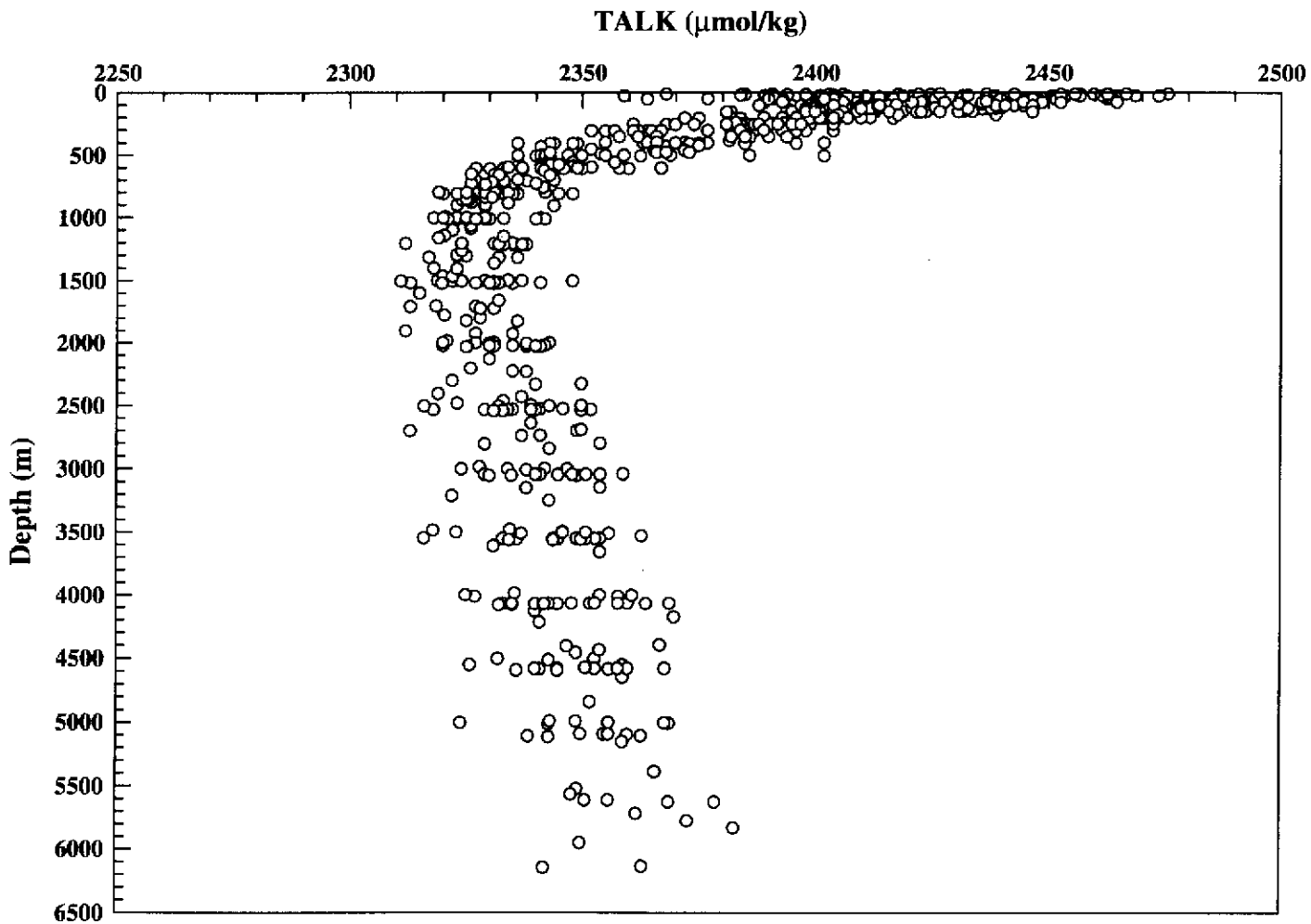

Fig. 4. Measured values of total alkalinity (TALK) vs depth for all stations.

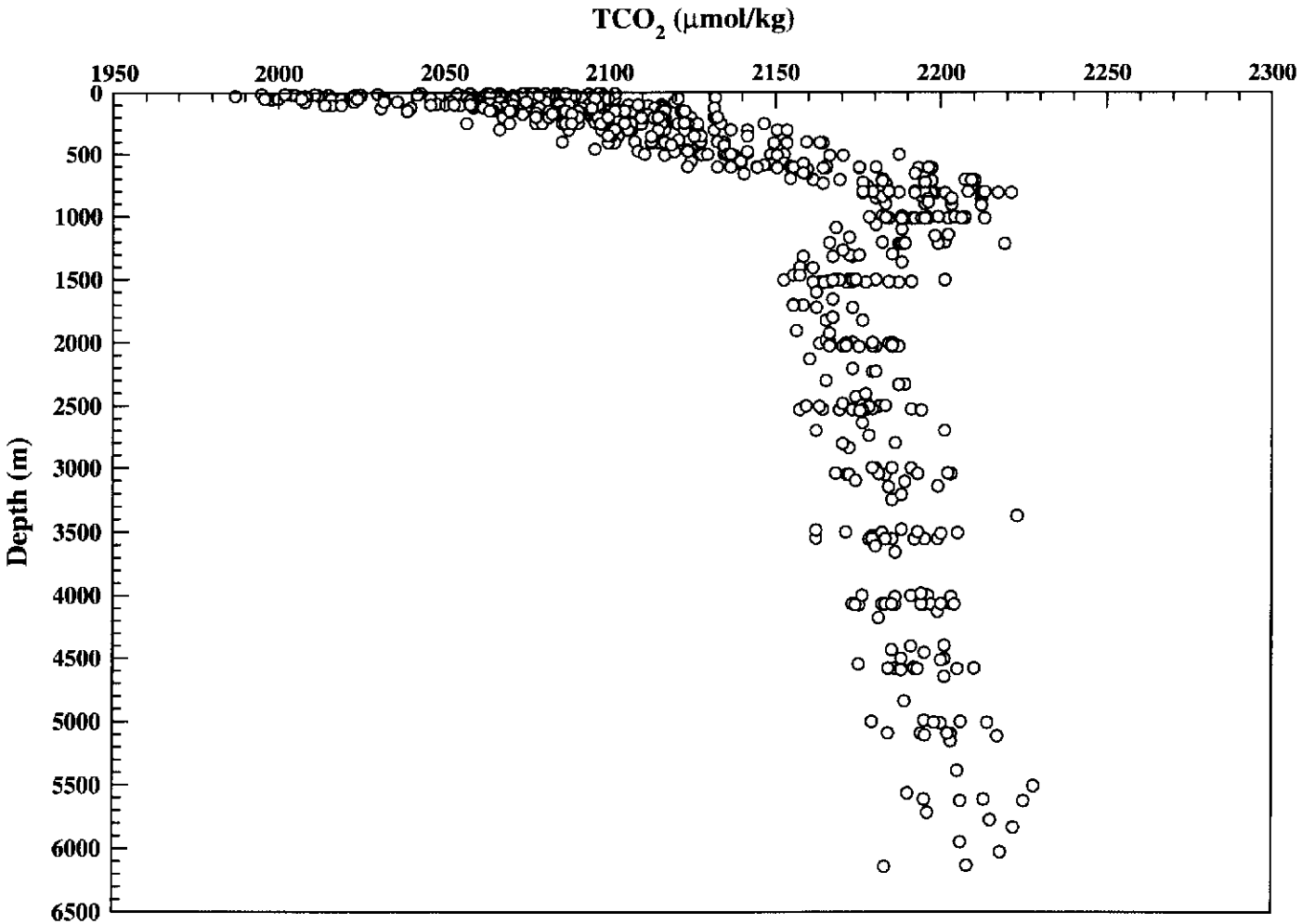

Fig. 5. Measured values of total carbon dioxide (TCO_2) vs depth for all stations.

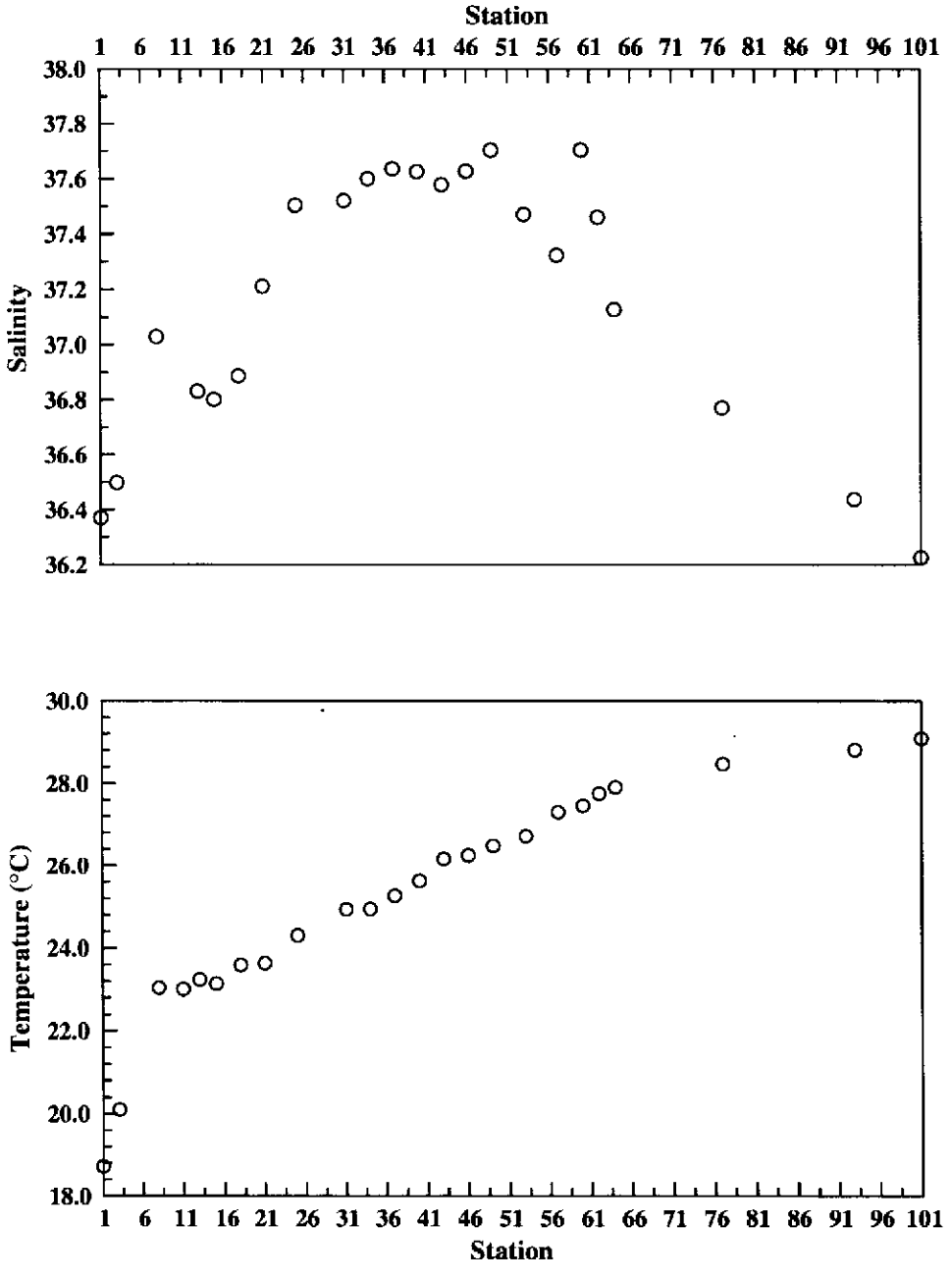

Fig. 6. Surface salinity and temperature vs station number.

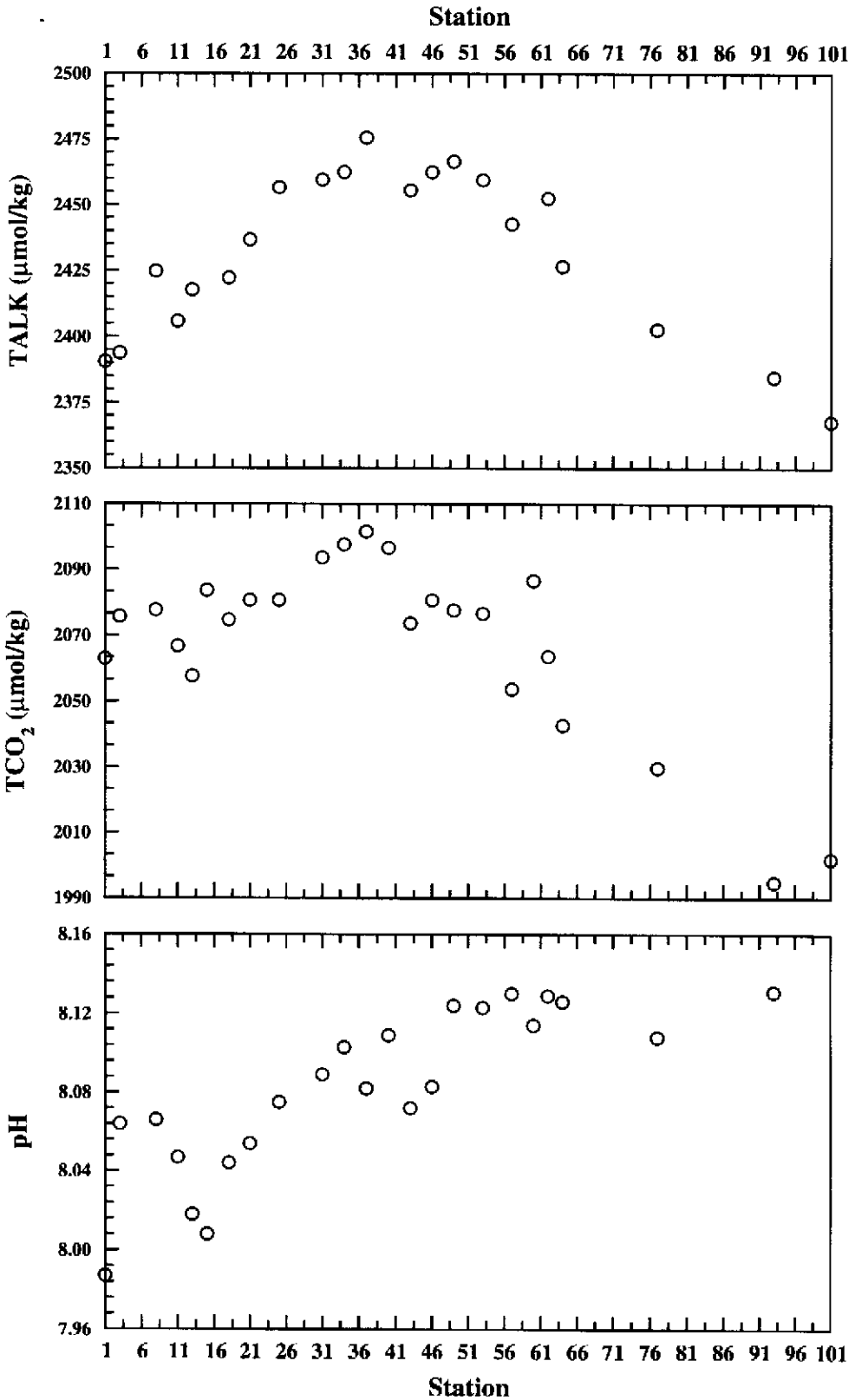

Fig. 7. Surface total alkalinity (TALK), total carbon dioxide (TCO_2), and pH vs station number.

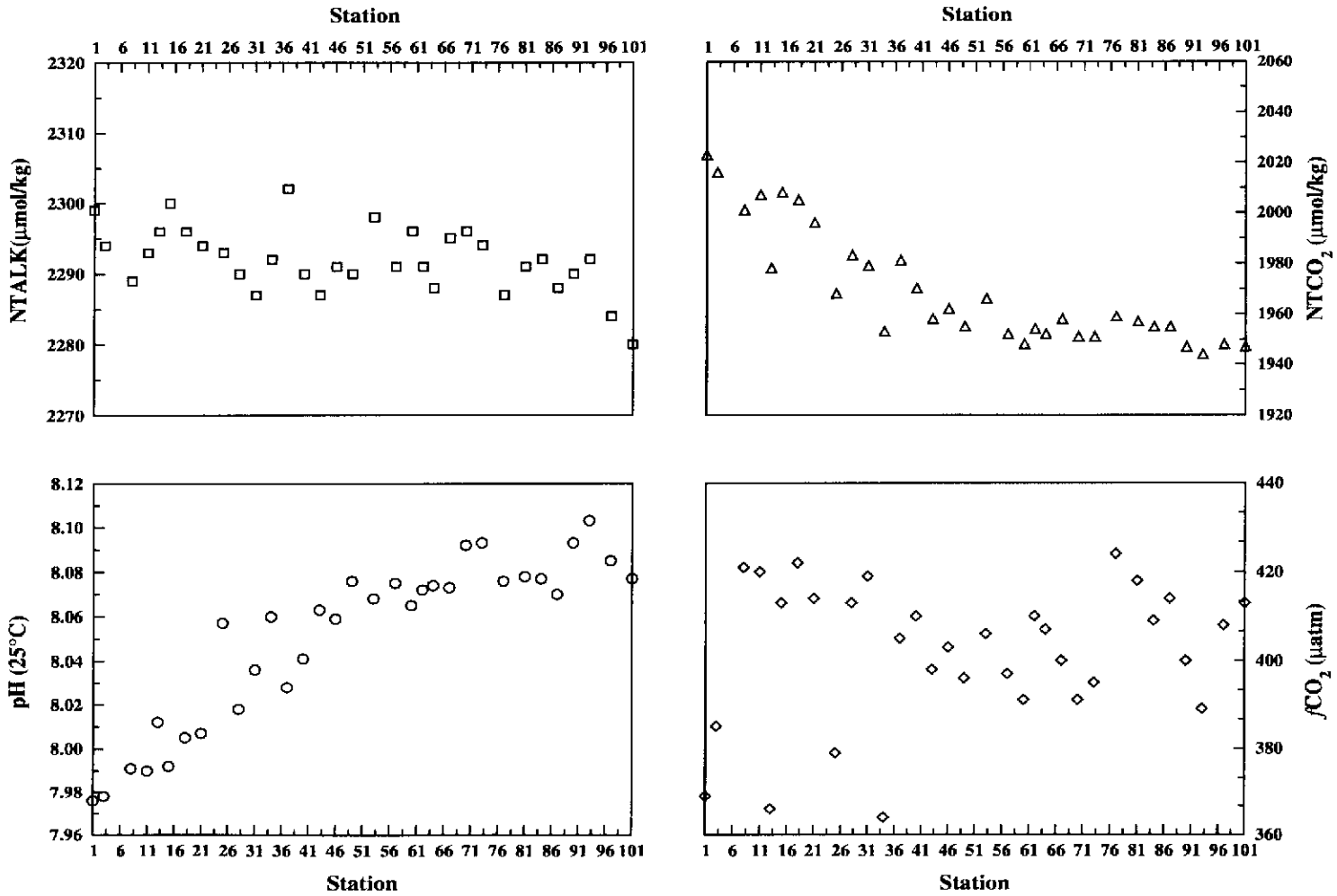

Fig. 8. Surface values of normalized TALK and TCO_2, pH at 25°C, and calculated fugacity of CO_2 (fCO_2) vs station number.

4. 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 A5 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, all 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.

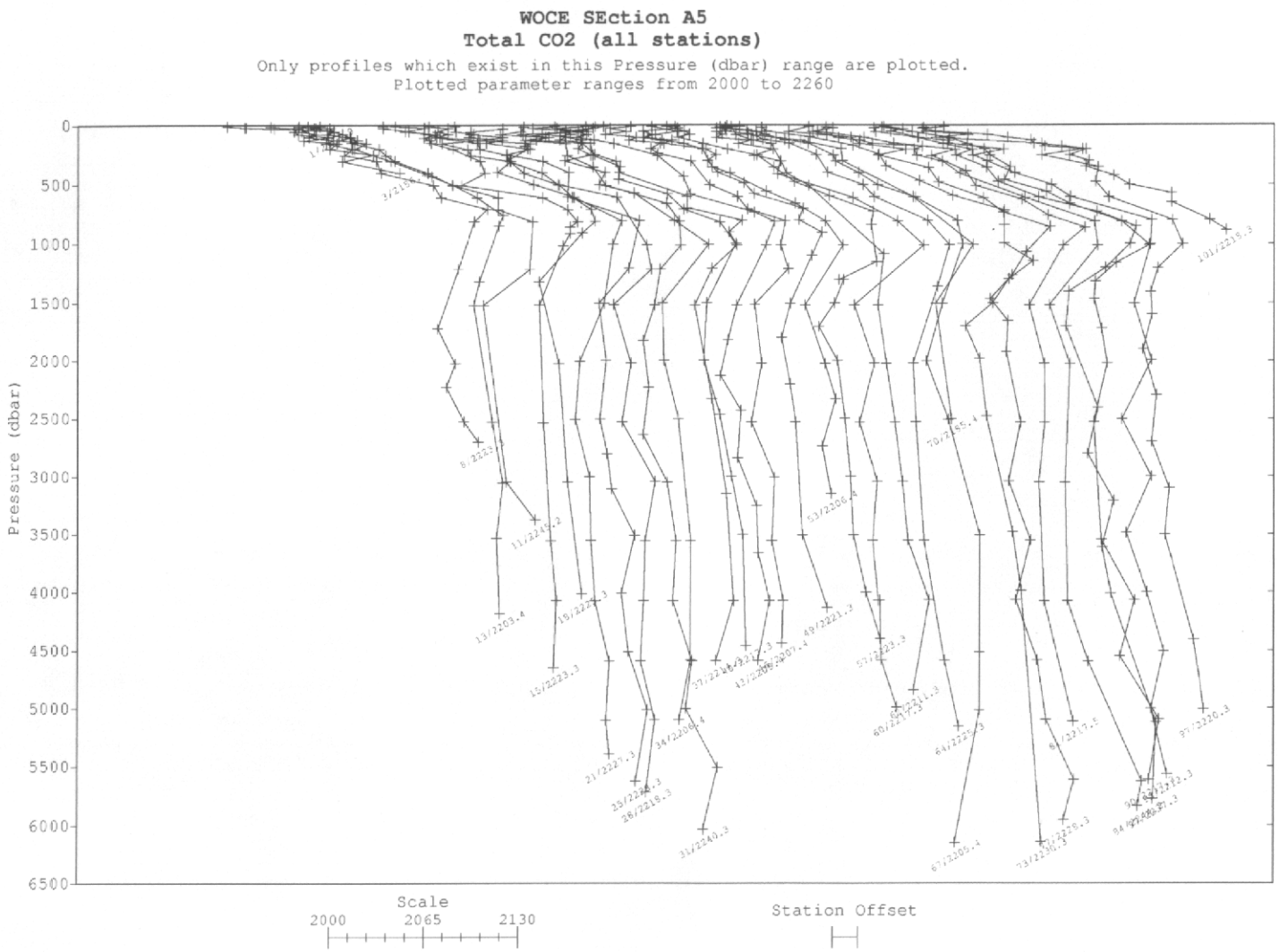

Fig. 9. Nested profiles: Total carbon dioxide (μmol/kg) vs pressure (dbar) for all stations of WOCE Section A5.

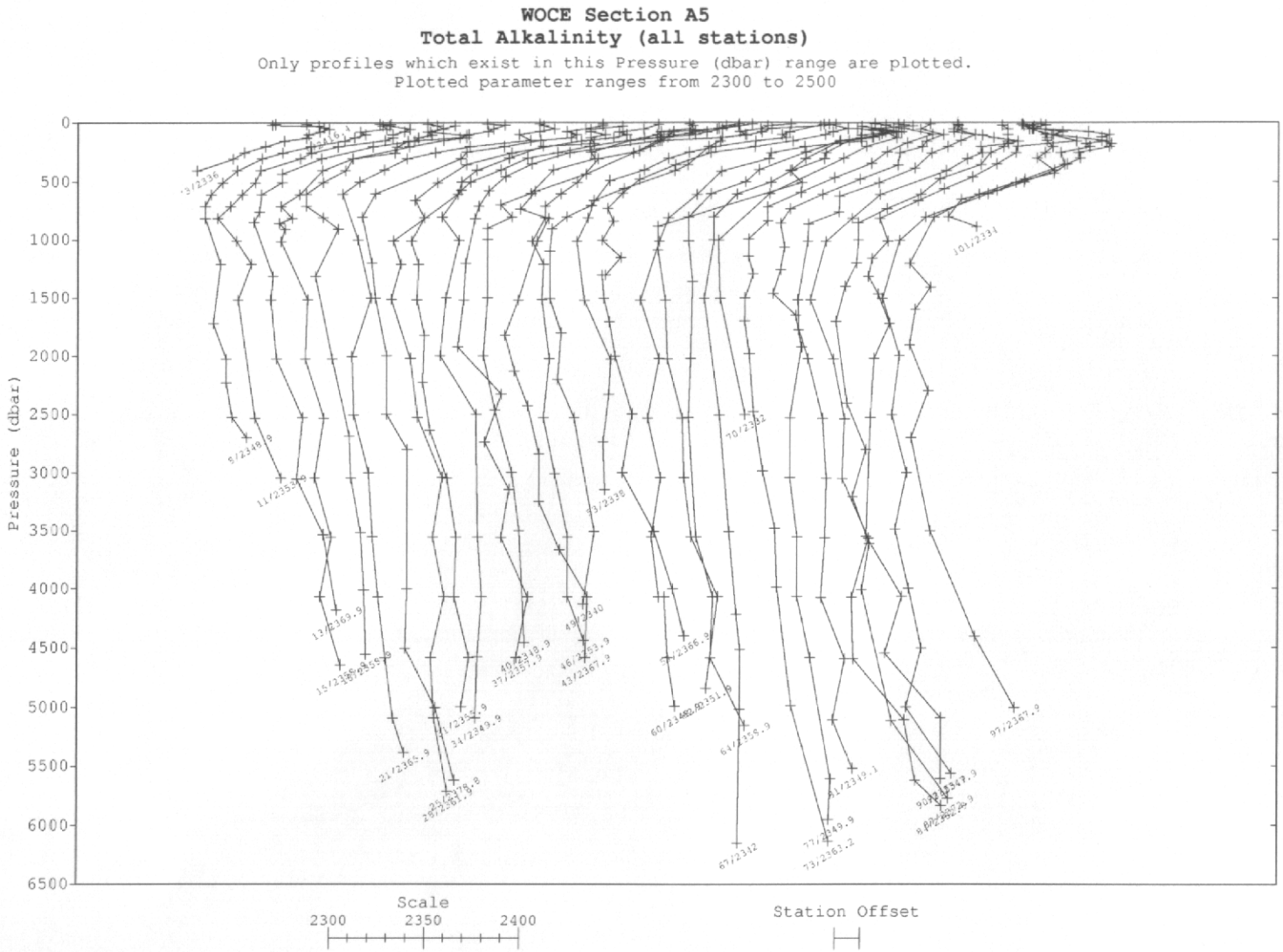

Fig. 10. Nested profiles: Total alkalinity (μmol/kg) vs pressure (dbar) for all stations of WOCE Section A5.

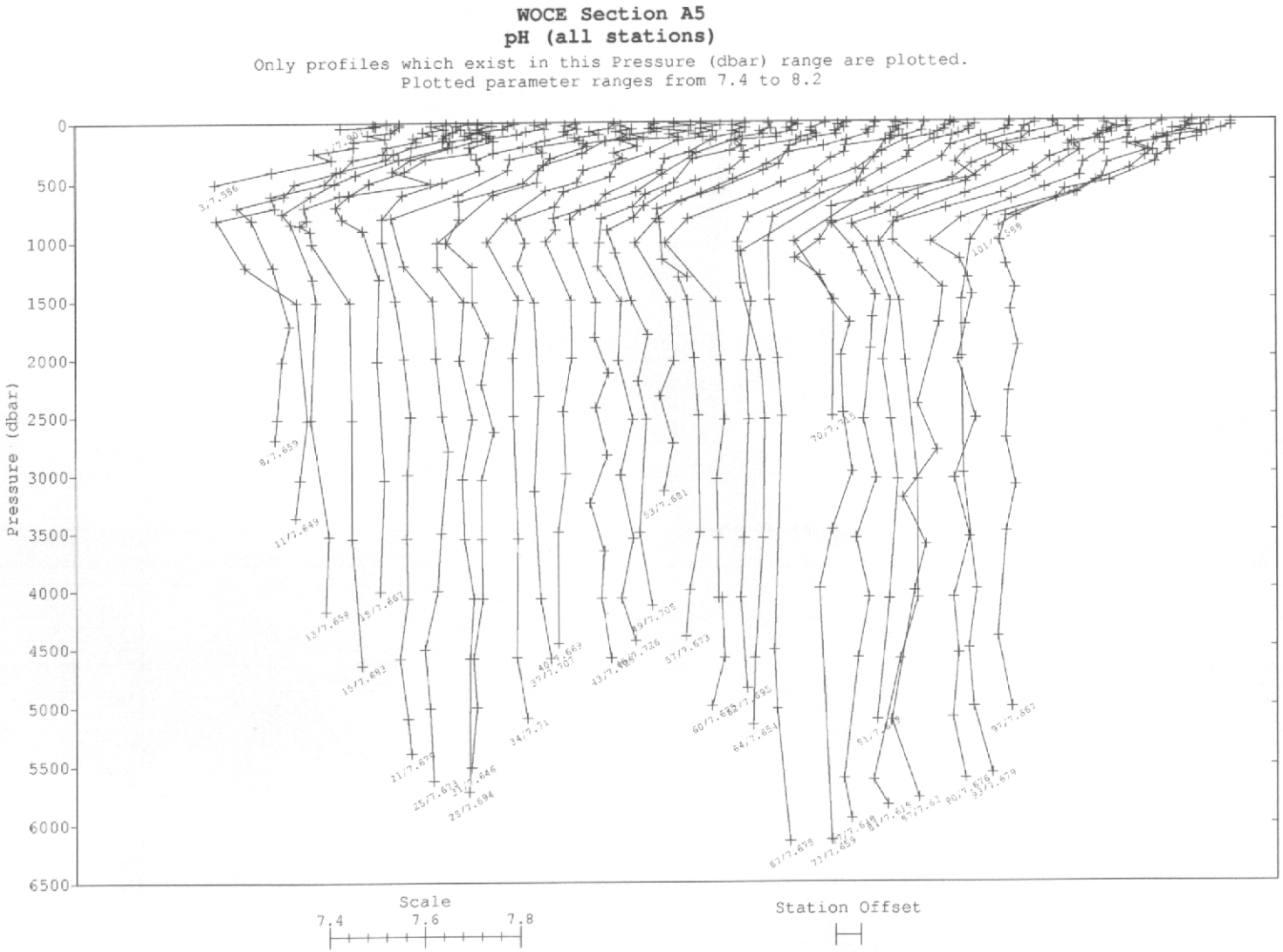

Fig. 11. Nested profiles: pH vs pressure (dbar) for all stations of WOCE Section A5.

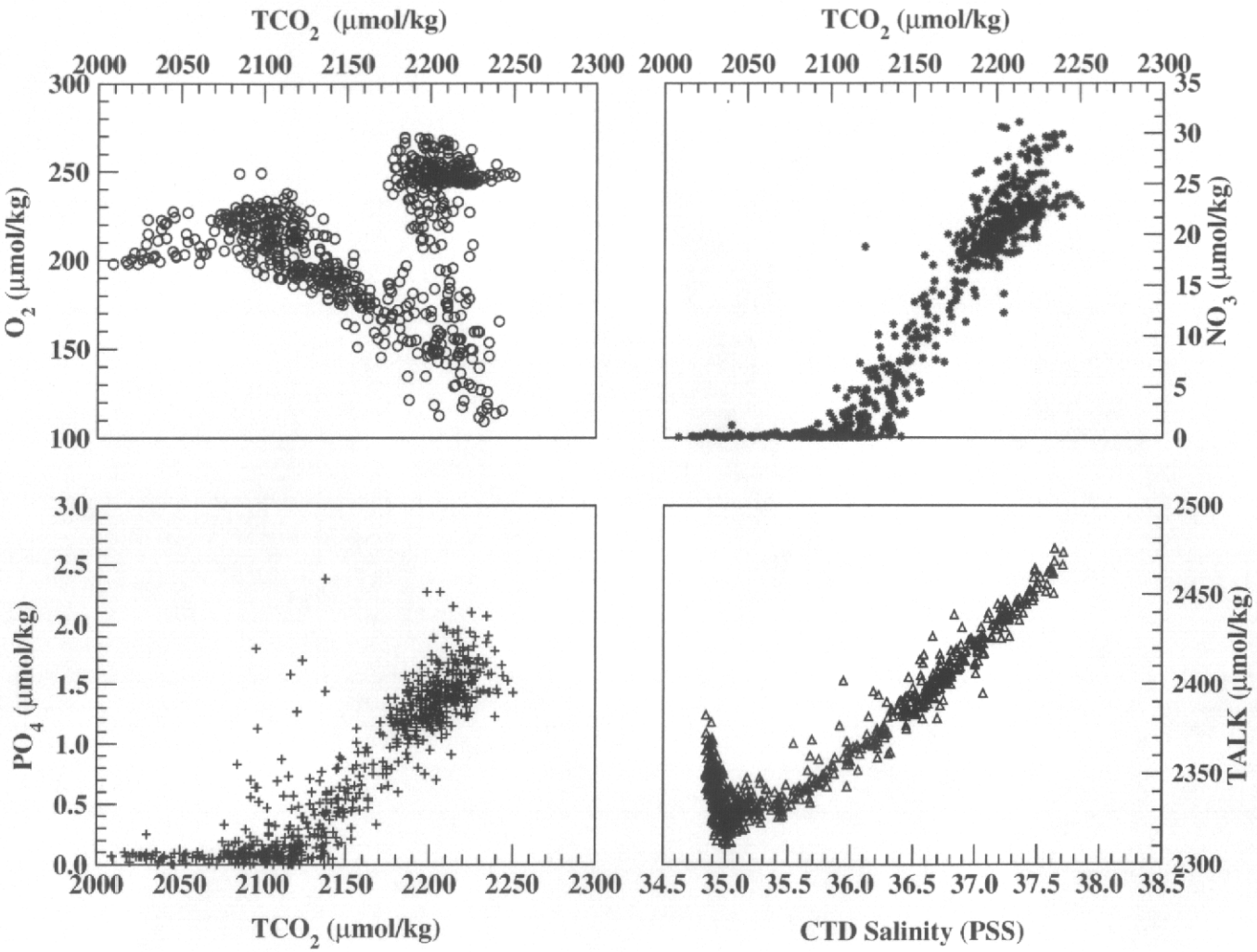

Fig. 12. Property-property plots for all stations occupied during R/V *Hespérides* Cruise HE06 (WOCE Section A5).

5. 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 cdiac.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

Internet: http://cdiac.esd.ornl.gov/

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PART 2:

CONTENT AND FORMAT OF DATA FILES

7. FILE DESCRIPTIONS

This section describes the content and format of each of the five files that comprise this NDP (see Table 5). Because CDIAC distributes the data set in several ways, (e.g., via anonymous FTP and on floppy diskette), each of the five files is referenced by both an ASCII file name, which is given in lowercase, bold-faced type (e.g., **ndp074.txt**) and a file number. The remainder of this section describes (or lists, where appropriate) the contents of each file.

Table 5. Content, size, and format of data files

File number, name, and description	Logical records	File size in bytes
1. **ndp074.txt:** a detailed description of the cruise, listings of the two provided FORTRAN 77 programs, and descriptions of the content and format of the two oceanographic files.	1,144	57,492
2. **stainv.for:** a FORTRAN 77 program to read and print **a5sta.dat** (file 4)	44	1,331
3. **a5dat.for:** a FORTRAN 77 program to read and print **a5.dat** (file 5)	53	2,070
4. **a5sta.dat:** a listing of the station locations, sampling dates, and sounding bottom depths for each of the 112 stations of WOCE Section A5.	123	9,593
5. **a5.dat:** hydrographic, carbon dioxide, and chemical data from the 112 stations occupied on WOCE Section A5.	2,487	401,604
Total	3,851	472,090

7.1 ndp074.txt (File 1)

This file contains a detailed description of the data set, listings of the two FORTRAN 77 programs used to read and print the data, and descriptions of the content and format of the two oceanographic data files. This file exists primarily for the benefit of individuals who acquire this database as machine-readable data files from CDIAC.

7.2 stainv.for (File 2)

This file contains a FORTRAN 77 program to read and print **a5sta.dat** (File 4). The following is a listing of this program. For additional information regarding variable definitions,

variable lengths, variable types, units, and codes, please see the description for **a5sta.dat** in Sect. 7.4.

```
c*****************************************************************
c* This is a Fortran 77 retrieval code to read and format the    *
c* station inventory file named a5sta.dat (File 4).              *
c*****************************************************************

c*Defines variables*

      INTEGER  stat, cast, depth
      REAL latdcm, londcm
      CHARACTER expo*8, sect*3, date*10, time*4
      OPEN (unit=1, file='a5sta.dat')
      OPEN (unit=2, file='a5stat.dat')
      write (2, 5)

c*Writes out column labels*

 5    format (4X, 'STATION INVENTORY: R/V HESPERIDES, WOCE A5',/,
     1 4X,'EXPOCODE',1X,'SECT',1X,'STNBR',2X,'CAST',
     2 9X,'DATE',2X,'TIME',3X,'LATITUDE',3X,'LONGITUDE',2X,
     3 'DEPTH',/)

c*Sets up a loop to read and format all the data in the file*

      read (1, 6)
 6    format (//////////)

 7    CONTINUE
      read (1, 10, end=999) expo, sect, stat, cast, date, time,
     1 latdcm, londcm, depth

 10   format (A12, 2X, A3, 3X, I3, 5X, I1, 3X, A10, 2X, A4, 4X,
     1 F7.3, 4X, F8.3, 3X, I4)

      write (2, 20) expo, sect, stat, cast, date, time,
     1 latdcm, londcm, depth

 20   format (A12, 2X, A3, 3X, I3, 5X, I1, 3X, A10, 2X, A4, 4X,
     1 F7.3, 4X, F8.3, 3X, I4)

      GOTO 7
 999  close(unit=5)
      close(unit=2)
      stop
      end
```

7.3 a5dat.for (File 3)

This file contains a FORTRAN 77 program to read and print **a5.dat** (File 5). The following is a listing of this program. For additional information regarding variable definitions, variable lengths, variable types, units, and codes, please see the description for **a5.dat** in Sect. 7.5.

```
c*****************************************************************
c* FORTRAN 77 data retrieval routine to read and print the       *
c* file named "a5.dat" (File 5).                                 *
c*****************************************************************
      CHARACTER qualt*12
      INTEGER sta, cast, samp, bot
      REAL pre, ctdtmp, ctdsal, ctdoxy, theta, sal, oxy, silca
```

```
      REAL nitrat, nitrit, phspht, talk, tcarb, ph
      OPEN (unit=1, file='a5.dat')

      OPEN (unit=2, file='a5data.dat')
      write (2, 5)

c*Writes out column labels*

 5    format (2X,'STNNBR',2X,'CASTNO',2X,'SAMPNO',2X,'BTLNBR',2X,
     1 'CTDPRS',2X,'CTDTMP',2X,'CTDSAL',3X,'CTDOXY',3X,'THETA',4X,
     2 'SALNTY',2X,'OXYGEN',2X,'SILCAT',2X,'NITRAT',2X,'NITRIT',2X,
     3 'PHSPHT',2X,'ALKALI',2X,'TCARBN',7X,'PH',7X,'QUALT1',/,
     5 36X,'DBAR',2X,'ITS-90',2X,'PSS-78',2X,'UMOL/KG',2X,'ITS-90',
     6 4X,'PSS-78',1X,'UMOL/KG',1X,6('UMOL/KG',1X),1X,'@25_DEG',12X,
     8 '*',/,25X,'*******',17X,2('*******',2X),9X,'*******',1X,
     8 7('*******',1X),1X,'*******',12X,'*')

c*Sets up a loop to read and format all the data in the file*

      read (1, 6)
 6    format (//////////////)

 7    CONTINUE
      read (1, 10, end=999) sta, cast, samp, bot, pre, ctdtmp,
     1 ctdsal, ctdoxy, theta, sal, oxy, silca, nitrat, nitrit,
     2 phspht, talk, tcarb, ph, qualt

 10   format (5X, I3, 7X, I1, 6X, I2, 6X, I2, 1X, F7.1, 1X, F7.4,
     1 1X, F7.4, 1X, F8.3, 1X, F7.4, 1X, F9.4, 1X, F7.1, 1X, F7.2,
     2 1X, F7.2, 1X, F7.2, 1X, F7.2, 1X, F7.1, 1X, F7.1, 1X, F8.3,
     3 1X, A12)

      write (2, 20) sta, cast, samp, bot, pre, ctdtmp,
     1 ctdsal, ctdoxy, theta, sal, oxy, silca, nitrat, nitrit,
     2 phspht, talk, tcarb, ph, qualt

 20   format (5X, I3, 7X, I1, 6X, I2, 6X, I2, 1X, F7.1, 1X, F7.4,
     1 1X, F7.4, 1X, F8.3, 1X, F7.4, 1X, F9.4, 1X, F7.1, 1X, F7.2,
     2 1X, F7.2, 1X, F7.2, 1X, F7.2, 1X, F7.1, 1X, F7.1, 1X, F8.3,
     3 1X, A12)

      GOTO 7
 999  close(unit=1)
      close(unit=2)
      stop
      end
```

7.4 a5sta.dat (File 4)

This file provides station inventory information for each of the 112 stations occupied during the R/V *Hespérides* cruise along WOCE Section A5. Each line of the file contains an expocode (expedition code unique to each cruise), section number, station number, cast number, sampling date (month/day/year), sampling time, latitude, longitude, and sounding depth. The file is sorted by station number and can be read by using the following FORTRAN 77 code (contained in **stainv.for**, File 2):

```
      INTEGER  stat, cast, depth
      REAL latdcm, londcm
      CHARACTER expo*8, sect*3, date*10, time*4

      read (1, 10, end=999) expo, sect, stat, cast, date, time,
```

```
     1 latdcm, londcm, depth

10     format (A12, 2X, A3, 3X, I3, 5X, I1, 3X, A10, 2X, A4, 4X,
     1 F7.3, 4X, F8.3, 3X, I4)
```

Stated in tabular form, the contents include the following:

Variable	Variable type	Variable width	Starting column	Ending column
expo	Character	12	1	12
sect	Character	3	15	17
stat	Numeric	3	21	23
cast	Numeric	1	29	29
date	Character	10	33	42
time	Character	4	45	48
latdcm	Numeric	7	53	59
londcm	Numeric	8	64	71
depth	Numeric	4	75	78

The variables are defined as follows:

expo is the unique expedition code of the cruise;

sect is the WOCE section number;

stat is the station number;

cast is the cast number;

date is the sampling date (month/day/year);

time is the sampling time [Greenwich mean time (GMT)];

latdcm is the latitude of the station (in decimal degrees; negative values indicate the Southern Hemisphere);

londcm is the longitude of the station (in decimal degrees; negative values indicate the Western Hemisphere);

depth is the sounding depth of the station (in meters).

7.5 a5.dat (File 5)

This file provides hydrographic, carbon dioxide, and chemical data for the 112 stations occupied during the R/V *Hespérides* cruise along WOCE Section A5. Each line consists of a station number, cast number, sample number, bottle number, CTD pressure, CTD temperature, CTD salinity, CTD oxygen, potential temperature, bottle salinity, oxygen, silicate, nitrate, nitrite, phosphate, total alkalinity, total CO_2, pH at 25°C, and data-quality flags. The file is sorted by station number and pressure and can be read by using the following FORTRAN 77 code (contained in **a5dat.for,** File 3):

```
      CHARACTER qualt*12
      INTEGER sta, cast, samp, bot
      REAL pre, ctdtmp, ctdsal, ctdoxy, theta, sal, oxy, silca
      REAL nitrat, nitrit, phspht, talk, tcarb, ph

      read (1, 10, end=999) sta, cast, samp, bot, pre, ctdtmp,
     1 ctdsal, ctdoxy, theta, sal, oxy, silca, nitrat, nitrit,
     2 phspht, talk, tcarb, ph, qualt


10    format (5X, I3, 7X, I1, 6X, I2, 6X, I2, 1X, F7.1, 1X, F7.4,
     1 1X, F7.4, 1X, F8.3, 1X, F7.4, 1X, F9.4, 1X, F7.1, 1X, F7.2,
     2 1X, F7.2, 1X, F7.2, 1X, F7.2, 1X, F7.1, 1X, F7.1, 1X, F8.3,
     3 1X, A12)
```

Stated in tabular form, the contents include the following:

Variable	Variable type	Variable width	Starting column	Ending column
sta	Numeric	3	6	8
cast	Numeric	1	16	16
samp	Numeric	2	23	24
bot	Numeric	2	31	32
pre	Numeric	7	34	40
ctdtmp	Numeric	7	42	48
ctdsal	Numeric	7	50	56
ctdoxy	Numeric	8	58	65
theta	Numeric	7	67	73
sal	Numeric	9	75	83
oxy	Numeric	7	85	91
silca	Numeric	7	93	99
nitrat	Numeric	7	101	107
nitrit	Numeric	7	109	115

Variable	Variable type	Variable width	Starting column	Ending column
phspht	Numeric	7	117	123
talk	Numeric	7	125	131
tcarb	Numeric	7	133	139
ph	Numeric	8	141	148
qualt	Character	12	150	161

The variables are defined as follows:

sta is the station number;

cast is the cast number;

samp is the sample number;

bot[a] is the bottle number;

pre is the CTD pressure (dbar);

ctdtmp is the CTD temperature (°C);

ctdsal[a] is the CTD salinity [on the Practical Salinity Scale (PSS)];

ctdoxy[a] is the CTD oxygen (μmol/kg);

theta is the potential temperature (°C);

sal[a] is the bottle salinity (on the PSS);

oxy[a] is the oxygen concentration (μmol/kg);

silca[a] is the silicate concentration (μmol/kg);

nitrat[a] is the nitrate concentration (μmol/kg);

nitrit[a] is the nitrite concentration (μmol/kg);

phspht[a] is the phosphate concentration (μmol/kg);

talk[a] is the total alkalinity concentration (μmol/kg);

tcarb[a] is the total carbon dioxide concentration (μmol/kg);

pH is the pH at 25°C;

qualt is a 12-digit character variable that contains data-quality flag codes for parameters underlined with asterisks (*******) in the file header.

---

[a]Variables that are underlined with asterisks in the data file's header indicate they have a data-quality flag. Data-quality flags are defined as follows:

1 = sample for this measurement was drawn from water bottle but analysis was not received;
2 = acceptable measurement;
3 = questionable measurement;
4 = bad measurement;
5 = not reported;
6 = mean of replicate measurements;
7 = manual chromatographic peak measurement;
8 = irregular digital chromatographic peak integration;
9 = sample not drawn for this measurement from this bottle.