ORNL/CDIAC-135
NDP-079

CARBON DIOXIDE, HYDROGRAPHIC, AND CHEMICAL DATA OBTAINED DURING THE R/V *METEOR* CRUISE 28/1 IN THE SOUTH ATLANTIC OCEAN (WOCE SECTION A8, MARCH 29 – MAY 12, 1994)

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Date Published: April 2002

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
Carbon Dioxide Information Analysis Center
OAK RIDGE NATIONAL LABORATORY
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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ACRONYMS

A/D	analog to digital
ADCP	acoustic Doppler current profiler
BAH	Biologische Anstalt Helgoland
BOD	biological oxygen demand
BMFT	Ministry of Research and Technology (Germany)
BNL	Brookhaven National Laboratory
^{14}C	radiocarbon
CALFAC	calibration factor
CDIAC	Carbon Dioxide Information Analysis Center
CFC	chlorofluorocarbon
CH_4	methane
CO_2	carbon dioxide
CTD	conductivity, temperature, and depth sensor
CRM	certified reference material
d.f.	degrees of freedom
DFG	German Research Foundation
DOE	U.S. Department of Energy
DHN	Diretoria Hidrografia eNavegacao, Brazil
DFG	German Research Foundation
DVS	Data collection and distribution system
DWD/SWA	German Weather Service / Sea Weather Office
fCO_2	fugacity of carbon dioxide
FID	flame ionization detector
FTP	file transfer protocol
GC	gas chromatograph
GMT	Greenwich mean time
GSV	gas sampling valve
H^3	Tritium
He	Helium
IAPSO	International Association for the Physical Sciences of the Ocean
IAPK	Institute of Applied Physics of the University of Kiel
IfMK	Institute für Meereskunde Universität Kiel
IO	input/output
IOS	Institute of Oceanographic Science, Wormley, UK
JGOFS	Joint Global Ocean Flux Study
N_2	gaseous nitrogen
nm	nautical mile
NDP	numeric data package
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
ONR	Office of Naval Research
OSU	Oregon State University
pc	personal computer
pCO_2	partial pressure of CO_2
PMEL	Pacific Marine Environmental Laboratory
PSS	Practical Salinity Scale

PU	Princeton University
QC-QA	quality control and quality assurance
QA	quality assurance
R/V	research vessel
RSMAS	Rosenstiel School of Marine and Atmospheric Sciences
SIO	Scripps Institution of Oceanography
SIS	Sensoren Instrumente Systeme
SOMMA	single-operator multi-parameter metabolic analyzer
TALK	total alkalinity
TCO_2	total carbon dioxide
TD	to deliver
VFC	voltage to frequency converter
WHOI	Woods Hole Oceanographic Institution
WHP	WOCE Hydrographic Program
WHPO	WOCE Hydrographic Program Office
WOCE	World Ocean Circulation Experiment
UBT	Universitat Bremen, Fachbereich Tracer Oceanographie
UMZ	University of Maiz
XBT	expendable bathythermographs
XCP	expendable current profiler

ABSTRACT

Johnson, K. M., K. Wills, A. Koertzinger, C. Neill, and D. W. R. Wallace. 2002. Carbon Dioxide, Hydrographic, and Chemical Data Obtained During the R/V *Meteo*r Cruise 28/1 in the South Atlantic Ocean (WOCE Section A8, March 29 – May 12, 1994), A. Kozyr and T.W. Beaty (ed.). ORNL/CDIAC-135, NDP-079. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, 50 pp.

This data documentation discusses the procedures and methods used to measure total carbon dioxide (TCO_2) and the fugacity of CO_2 (fCO_2) at hydrographic stations during the R/V *Meteor* oceanographic cruise 28/1 in the South Atlantic Ocean (Section A8). Conducted as part of the World Ocean Circulation Experiment (WOCE), the cruise began in Recife, Brazil, on March 29, 1994, and ended after 35 days at sea in Walvis Bay, Namibia, on May 12, 1994. Instructions for accessing the data are provided.

TCO_2 was measured using two single-operator multiparameter metabolic analyzers (SOMMA) coupled to a coulometer for extracting and detecting CO_2 from seawater samples. The overall precision and accuracy of the analyses was ±1.17 Fmol/kg. For the second carbonate system parameter, the fCO_2 was measured in discrete samples by equilibrating a known volume of liquid phase (seawater) with a known volume of a gas phase containing a known mixture of CO_2 in gaseous nitrogen (N_2). After equilibration, the gas phase CO_2 concentration was determined by flame ionization detection following the catalytic conversion of CO_2 to methane (CH_4). The precision of these measurements was less than or equal to 1.0%.

The R/V *Meteor* Cruise 28/1 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 90 data retrieval routine files, a readme file, and this printed documentation that describes the contents and format of all files as well as the procedures and methods used to obtain the data.

Keywords: carbon dioxide; coulometry; World Ocean Circulation Experiment; South Atlantic Ocean; hydrographic measurements; total carbon dioxide; fugacity of CO_2; carbon cycle.

PART 1:

OVERVIEW

1. BACKGROUND INFORMATION

The World Ocean Circulation Experiment (WOCE) Hydrographic Program (WHP) was a major component of the World Climate Research Program, whose overall goal was to better understand the ocean's role in climate and climatic changes resulting from both natural and anthropogenic causes. The need for this experiment arose from serious concern over the rising atmospheric concentrations of carbon dioxide (CO_2) and their effect on the heat balance of the global atmosphere. The increasing concentrations of these gases may intensify the earth's natural greenhouse effect and alter the global climate in ways that are not well understood. Carbon in the oceans is poorly characterized and unevenly distributed because of complex circulation patterns and biogeochemical cycles. Although total carbon dioxide (TCO_2) was not an official WOCE measurement, a coordinated effort, supported in the United States by the Department of Energy (DOE) and the National Oceanic and Atmospheric Administration (NOAA), was made on WOCE cruises through 1998 to measure the global, spatial, and temporal distributions of TCO_2 and other related parameters. The two primary objectives of this effort were to estimate the meridional transport of inorganic carbon in a manner analogous to the estimates of oceanic heat transport (Bryden and Hall 1980; Brewer et al. 1989; Holfort et al. 1998; Roemmich and Wunsch 1985) and to build a database suitable for carbon-cycle modeling and the estimation of anthropogenic CO_2 increase in the oceans. The CO_2 Survey took advantage of the sampling opportunities provided by the WHP cruises during this period, and the final data set is expected to cover on the order of 23,000 stations. Wallace (2001) has recently reviewed the goals, conduct, and initial findings of the Joint Global Ocean Flux Study (JGOFS)/WOCE Global CO_2 Survey.

This report discusses the carbonate system parameters, TCO_2 and the fugacity of CO_2 ($f\mathrm{CO}_2$), measured aboard the research vessel (R/V) *Meteor* during Cruise 28, Leg 1, along the WOCE Zonal Section A8. This Section began in Recife, Brazil, on March 29, and ended in Walvis Bay, Namibia, on May 10, 1994 (Fig. 1). This is the concluding section of the four contiguous zonal sections completed in the South Atlantic (A9, A10, A11, and A8) during the WOCE Survey. Scientists from the Brookhaven National Laboratory (BNL) participated in the cruises of these three sections (A9, A10, and A8). The A8 Section cruise continued the tradition whereby personnel from BNL and the CO_2 group at the Institut für Meereskunde Universität Kiel (IfMK) collaborated to make the CO_2 measurements aboard the R/V *Meteor*. From this section, the large-scale three-dimensional distribution of temperature, salinity, and chemical constituents, including the carbonate system parameters, can be mapped. Knowledge of these parameters and their initial conditions will allow heat, water, and carbon transports to be determined. An understanding of these transports will contribute to the understanding of processes that are relevant for climate change. This concluding section in the subtropical South Atlantic Ocean is especially relevant to CO_2 transport because it crosses both the Brazil and the Benguela Boundary Currents. An analysis of these data has been published in Holfort et al. (1998).

The work aboard the R/V *Meteor* was supported by the U.S. DOE under contract DE-ACO2-76CH00016. The authors are grateful to the Sonderforschungsbereich 460 at the University of Kiel, which was lead by Dr. F. Schott and funded by the Deutsche Forschungsgemeinschaft, for their support and assistance in completing the written documentation.

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Fig. 1. The cruise track during the R/V *Meteor* Cruise 28/1 in the South Atlantic Ocean along WOCE Section A8. This figure was produced by the Ocean Data View program (Schlitzer 2001).

2. DESCRIPTION OF THE EXPEDITION

2.1 R/V *Meteor*: Technical Details and History

The R/V *Meteor* is owned by the Federal Republic of Germany through the Ministry of Research and Technology (BMFT), which financed its construction. It is operated by the German Research Foundation (DFG), which provides about 70% of its operating funds (the BMFT supplies the remainder). DFG also plans the scientific cruises and appoints the chief scientists. The Operations Control Office of the University of Hamburg is responsible for management, logistics, execution, and supervision of ship operations. These functions are exercised by direct cooperation with expedition coordinators and the managing owners, the Reedereigemeinschaft Forschungsschiffahrt GmbH, located in Bremen, Germany. The latter is responsible for hiring, provisioning, and coordinating ship maintenance. Used for ocean research, primarily in the Atlantic and Indian Oceans, the R/V *Meteor* routinely carries scientists from many different countries. The *Meteor* was completed in 1986 in Travemunde, Germany. Table 1 provides a list of the basic features of the R/V Meteor, while Table 2 illustrates general cruise information.

The *Meteor* (I) was constructed in 1925, and was the first research and survey vessel of that name. Owned by the German navy, it was based in Wilhelmshaven. One of its first expeditions was the German Atlantic Ocean Expedition of 1925–1927, which was organized by the Institute of Marine Research in Berlin. Thereafter, the vessel was used for German physical, chemical, and microbiological marine investigations and for navy surveying and fisheries protection duties.

The *Meteor* (II) was planned in the early 1960s. It was operated by the Deutsche Forschungsgemeinschaft (German Science Community) in Bad Godesberg and the Deutsches Hydrographisches Institut (German Hydrographic Institute) in Hamburg. In 1964, the *Meteor* (II) was commissioned to participate in the International Indian Ocean Expedition.

The multipurpose *Meteor* (III), used for the cruise described in this documentation, was completed in 1986, replacing *Meteor* (II). Based in Hamburg, its purpose is German ocean research worldwide and cooperative efforts with other nations in this field. The vessel serves scientists of all marine disciplines and sails in all of the world's oceans.

2.2 Brief Cruise Summary

Originally, the R/V *Meteor* Cruise 28/1 was scheduled to terminate at Pointe Noir in the Republic of the Congo. However, unknown to the responsible German authorities, the U.S. State Department had issued a travel warning urging Americans to defer travel to the Congo! K. M. Johnson of BNL forwarded this warning to Dr. Walter Zenk of IfMK, who confirmed the warning with the German government. After a furious exchange of faxes, the *Meteor* team was informed that the final cruise destination (i.e., termination point) was changed to Walvis Bay, Namibia, which had just been transferred from the Republic of South Africa to Namibia a few days earlier. Johnson arrived in Recife on March 27, 1994, where he was joined by BNL CO_2

group members Craig Neill and Kevin Wills. The CO_2 group boarded the R/V *Meteor* on March 28 and immediately began to set the instruments up. The two SOMMA-coulometry systems along with the discrete fCO_2 system were located in the *Meteor*'s universal laboratory adjacent to the geo-laboratory.

Table 1. Characteristics of the R/V *Meteor*

Ship name:	R/V *Meteor*
Call sign:	DBBH
Port of registration:	Hamburg
Classification:	GL+100A4E2+MC Auto
Operator:	University of Hamburg, Institute for Ocean Research
Built:	1985 and 1986 at Schlichting Werft, Travemunde
Basic dimensions:	

Gross registered tonnage:	3990	Beam:	16.50 m
Net registered tonnage:	1284	Draugth maximum:	5.60 m
Displacement:	4780 t	Service speed:	12 kn
Length overall:	97.50 m	Depth main deck:	7.70m

Personnel	Crew: 32, Scientists: 30
Main engine	4 × Mak6M 322 = 4 × 1000 kW at 750 rpm
Propulsion	Diesel-electrical, tandem-motor = 2 × 1150 kW
Fuel consumption	Approximately 12.0 t IFO-80 per day at the service Speed
Maximum cruise duration	60 days
Nautical equipment :	Integrated navigation system with data transfer to position computer, echo sounder synchronization and supervision, and data-processing facility
Science quarters:	20 laboratories on the main deck with ~400 m^2 of working space for multidiciplinary research

Table 2. R/V Meteor Cruise 28/1 Information

Ship name: *Meteor*

Cruise/leg: Cruise No. 28/1

Ports of call: Recife, Brazil
Walvis Bay, Namibia

Dates: March 29 to May 10, 1994

Funding support: U.S. DOE
Deutsche Forschungsgemeinschaft

Chief scientist: Dr. Thomas Mueller, IfMK

Master: Hartmut Andresen

Parameter	Institution[a]	Responsible personnel
conductivity, temperature, and depth sensor (CTD), and salinity	IfMK	T. Mueller P. Beining P. Meyer
Nutrients	IOS	D. Hydes
Oxygen (O_2)	IOS	D. Hydes
Chloroflurocarbon (CFC)	UBT	A. Putzka
Tritium (H^3), helium (He), and radiocarbon(^{14}C)	UBT	A. Putzka
Total Carbon Dioxide (TCO_2)	BNL	K.M. Johnson D.W.R. Wallace K.D. Wills
Fugacity of CO_2 (fCO_2)	BNL	C. Neill D.R.W. Wallace K.M. Johnson
Acoustic Doppler current profiler (ADCP)	IfMK	T. Mueller
Atmospheric physics	UMZ	J. Brinkmann
Ichthyoplankton	BAH	C. Zelck
Meteorology	DWD/SWA	K. Flechsenhar
Current meter (towed)	IAPK	R. Thomas
Brazilian observer	DHN	R. Campos

[a] Participating Institutions: Biologische Anstalt Helgoland (BAH); Brookhaven National Laboratory (BNL); Diretoria Hidrografia e Navegacao, Brazil (DHN); German Weather Service / Sea Weather Office (DWD/SWA); Institute of Applied Physics of the University of Kiel (IAPK); Institute für Meereskunde der Universität Kiel (IfMK); Institute of Oceanographic Sciences, Wormley, UK (IOS); Universität Bremen, Fachbereich Tracer Oceanographie (UBT); and Institute for Physics and Atomsphere, University of Mainz (UMZ).

The R/V *Meteor* departed Recife, Brazil, on March 29 at approximately 2 p.m. local time. Work began after crossing the twelfth nautical mile (12-nm) zone of Brazil when the underway recording systems (the towed Geomagnetic Electro Kinetograph, the acoustic Doppler current profiler, and the navigational data system) were switched on. Test stations (Stations 165 through 168) were taken the first two days of the cruise to set up and test the CO_2 instruments. WOCE Section A8 began with station 169 outside the 12-nm zone of Brazil on April 1, at 10E 03' S and 35E 46' W on the 200-m depth contour. Subsequent stations at intervals of from 5 to 20 nm were taken until Station 181 at the nominal latitude of 11E 20' S and 34E 00' W. After Station 181, the station interval was increased to 30 nm until station 185 (32E W) and increased to 38 nm thereafter (beyond the 200-nm economic zone of Brazil). Prior to the 200-nm zone, sampling usually included plankton tows, but their frequency decreased in the open ocean waters to every 70 to 90 nm. Station spacing was narrowed to 30 nm as the ship approached the Mid-Atlantic Ridge (Stations 200–210) and then narrowed to 24 nm over the ridge (until Station 222). The African continental break at 8E E was reached at Station 260, whereby 28 nm spacing was sampled until 10E E was reached at Station 264 at the 200-nm economic zone of Angola. The CTD section work continued until Station 274 at the 50 nm zone. While waiting for further clearance, the northern part of a box around the eastern tail of A8 was surveyed using the CTD/ADCP system down to 1000 m. When clearance came, two days later, the R/V *Meteor* resumed the A8 section at 11E 20' S and 13E 05' E on Station 287 and completed the section on the 200-m depth contour with Station 290 on May 7. The ship arrived at Walvis Bay on May 10. Apart from some showers on April 9, a small swell (2 to 3 m) between April 10 and 19, and fog off of the Angola coast due to cold upwelling waters, the weather remained mostly sunny with summer temperatures and relatively calm seas. Of special note was the very excellent Easter repast prepared for the R/V *Meteor* team by the galley staff which featured pheasant, smoked salmon, venison, and many other delicacies.

Two single-operator multi-parameter metabolic analyzers (SOMMA) were used on this cruise. One was supplied by BNL (serial No. 004) and the other by the IfMK (serial No. 014). In addition, a gas chromatographic (GC)-based system for measuring discrete $f\mathrm{CO}_2$ was deployed. The CO_2 samples were drawn in conjunction with tracer samples from 51 of 108 WOCE CTD stations (47% coverage) occupied during the cruise (Fig 2). As on previous cruises, not all stations could be sampled for TCO_2 and $f\mathrm{CO}_2$ because of the time required for analysis. However, the goal of approximately 50% coverage was attained. The standard WOCE parameters (temperature, oxygen, nutrients, and salinity) were analyzed on all samples. The tracer samples included chloroflurocarbons (CFCs), helium (He), tritium (H^3), and radiocarbon (^{14}C).

Analytical problems were confined mostly to damage during transit. A pipette along with a jacketed sample bath were broken, but replacements were available on board ship for these items. Some of the refrigerated baths used for thermostating the instruments (particularly the $f\mathrm{CO}_2$ shaking bath) labored under the limitations of the 50-cps power aboard the R/V *Meteor*. One bath caught fire and was destroyed. The gas calibration hardware functioned throughout the cruise on both SOMMA systems (004 and 014). Downtime for both systems was limited to the time required to change the cells and a few incidents requiring minor adjustments to hardware or software. The CO_2 measurement team deployed on this cruise probably represents one of the most experienced analytical groups ever assembled for a single cruise. A brief look at the references will confirm the collective contributions of the measurement group to the accurate determination of dissolved CO_2 in seawater before and during the WOCE CO_2 Survey.

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Fig. 2. Sampling depths at all hydrographic stations occupied during the R/V *Meteor* Cruise 28/1 along WOCE Section A8.

3. DESCRIPTION OF VARIABLES AND METHODS

3.1 Hydrographic Measurements

Water samples were collected in twenty-four 10-L Niskin bottles attached to a general oceanic rosette sampler mounted on a Neil Brown Mark III CTD (MKIIIB) provided by the IfMK (Brown and Morrison 1978). All stations were profiled to within 5 to 10 m of the bottom with the CTD. The Niskin bottles were closed 10 m from the bottom for the chemical samples, and the last two bottles were closed in the mixed layer near the surface at a depth of approximately 10 m. The closing depths for the remaining bottles varied. During two successive stations the bottles were closed at fixed depths, and then for the next two stations, the closing depths were set midway between those of the preceding two profiles (see Fig. 2). This was done to ensure that contour plots of the chemical parameters would not miss any significant water column features. The prescribed WOCE sample order was followed: CFCs, helium (He), oxygen (O_2), CO_2, nutrients, tritium (H^3), and salinity. For stations greater than 3500 m in depth, two separate CTD/rosette casts were made to get adequate coverage (n = 36). For stations less than 3500 m, one CTD/rosette cast of up to 24 bottles was made. Surface currents down to 1000 m, surface temperature, and surface salinity were measured continually during the cruise with a hull-mounted ADCP. Near-surface (approximately 4 m) temperature and salinity were measured continually by the ship's data collection and distribution system (DVS) and integrated with the ship's navigation data (position). The ship's position was updated every two minutes. In between CTD stations, expendable bathythermographs (XBTs) were routinely launched. Over the boundary currents XBTs were launched every half hour, and the XBT launches were supplemented with free-falling expendable current profilers (XCP).

No serious problems were experienced with the CTD/rosette systems during this cruise. Repeated checks on board and several careful verifications using the complete bottle data sets were carried out. Pre-cruise calibrations of pressure and temperature for both CTDs were performed in November 1993 at IfMK's calibration laboratory and are described in Saunders et al. (1991). For these calibrations, a Rosemount Pt25 resistance from Sensoren Instrumente Systeme (SIS, Kiel) was used to convert the CTD temperature output to the international temperature scale of 1990 (ITS90), which is bound at the melting points of water and gallium (0.01EC and 28EC, respectively). Comparisons of the CTD temperature output with three electronic reversing thermometers (SIS, Kiel) were made during the cruise, and no drift in the CTD sensor was observed. Based on these data and the pre-cruise calibration, temperature is thought to be accurate to within ± 2 mK, and pressure good to 2 dbar or better.

Salinity calibrations were made using a bottle salinity measured one to two days after collection on a Guildline Autosal model 8400A that was calibrated with standard seawater (batch P120). The precision of the salinity determination was ± 0.0005, and the drift of the salinometer over the whole cruise did not exceed 0.0005. The accuracy of the bottle data was ± 0.0015 and the CTD data yielded an accuracy of ± 0.002. Bottle **oxygen, nitrate, nitrite, and silicate** were determined on every bottle closed on the A8 section. Not counting duplicates, some 3700 samples were analyzed. Oxygen was determined by Winkler titration after the technique of Culberson and Huang (1987) using a Metrohm Titrino with the end point determined amperometrically. The calculation of oxygen concentrations followed the procedure outlined in the *WOCE Manual of Operations and Methods* (Culberson and Williams 1991). Appropriate corrections for sample density, blanks, and volumetric expansion have been included. The precision of the analyses, defined as the mean of the absolute differences from duplicate samples drawn from the same Niskin bottles during the cruise, was ± 1.12 µmol/kg (*n* = 559). The concentrations of nitrate, nitrite, and silicate dissolved in seawater were determined on samples collected in virgin polystyrene 30 mL vials, on an autoanalyzer (Chemlab AAII) according to procedures given by Grasshoff (1976), Hydes (1984), and Hydes and Hill (1985). Phosphate could not be measured because the sensitivity of the analyzer was too low. Samples were stored at 4EC until analyzed (i.e., within 12 hours of collection). Precision for silicate was ± 0.2 to ± 0.3 µmol/kg (*n* = 594); and for both nitrite and nitrate, the precision was ± 0.1 to ± 0.1 µmol/kg (*n* = 594). Preweighed standards were used to prepare the nutrient working standards on board the ship. In the case of silicate, the shipboard standards were compared with a standard solution prepared in a laboratory before the cruise. No significant differences were noted. For accuracy, a nutrient standard solution (from Sagami Chemical Co.) was used as the certified reference material (CRM). New bottles of the standard were opened each week and analyzed. The results were: nitrate 9.76 ± 0.14 µmol/kg (*n* = 36) and silicate 49.70 ± 0.4 µmol/kg (n = 27). The known concentrations were 10.0 and 50.0 µmol/kg, respectively.

3.2 Total Carbon Dioxide Measurements

The TCO_2 was determined using two automated dynamic headspace SOMMA sample processors with coulometric detection of the CO_2 extracted from acidified samples. A description of the SOMMA-coulometry system and its calibration can be found in Johnson et al. (1987); Johnson and Wallace (1992); and Johnson et al. (1993). A schematic diagram of the SOMMA analytical system and sequence may be found in Johnson et al. (1993), and further details concerning the coulometric titration can be found in Huffman (1977) and Johnson et al. (1985). Samples were collected in 300-mL precombusted (450EC for 24 h) glass standard biological oxygen demand (BOD) bottles, poisoned with 200 FL of a 50% saturated solution of mercury chloride ($HgCl_2$), and analyzed for TCO_2 within 24 hours of collection (*Handbook of Methods*, DOE 1994). The samples were stored in a refrigerator in darkness at approximately 15EC until analyzed. Analyses of duplicate samples separated in time by up to 8 hours showed no evidence of any significant biological consumption or production of CO_2 during storage under these conditions. CRMs were routinely analyzed according to the DOE handbook (1994). The CRMs were supplied by Dr. Andrew Dickson of the Scripps Institution of Oceanography (SIO), and for this cruise batch 21 was used with a salinity of 34.54 and a certified TCO_2 of 1991.94 ± 0.79 Fmol/kg. The CRM TCO_2 concentration was determined by vacuum extraction and manometry in the laboratory of C. D. Keeling at SIO. Some CRM were lost in transit probably as a result of overheating which compromised the bottle seals. However, most of the damaged seals could be seen with the naked eye, therefore effort was made to carefully inspect and analyze only uncompromised CRM.

Seawater was introduced into an acidified stripping chamber from an automated “to-deliver” (TD) pipette. The resultant CO_2 from continuous gas extraction was dried and coulometrically titrated on a model 5011 UIC coulometer. The coulometer was adjusted to give a maximum titration current of 50 mA, and the samples were run in counts mode. In counts mode, the number of pulses or counts generated during the titration by the coulometer’s voltage to frequency converter (VFC) are recorded and displayed on a personal computer (PC). In each coulometer cell, the acid, hydroxyethylcarbamic acid [HO(CH_2)2NHCOOH], formed from the reaction of CO_2 and ethanolamine (C_2H_7NO), is titrated coulometrically to electrolytically generate hydroxyl ions (OH^-) with photometric endpoint detection. The product of the time and the current passed through the cell during this titration (charge in coulombs) is related by Faraday’s constant to the number of moles of OH- generated and thus to the moles of CO_2 that reacted with ethanolamine to form the acid. The age of each titration cell is logged from its birth, which is the time that electrical current is applied to the cell, until its death, which is the time when the current is turned off. The age is measured as chronological age in minutes from birth and in mg of carbon (mgC) titrated since birth (i. e., carbon age).

Each system was controlled with an IBM-compatible PC equipped with two RS232 serial ports for the coulometer and barometer, a 24-line digital input/output (I/O) card for the solid state relays and valves, and an analog to digital (A/D) card for the temperature, conductivity, and pressure sensors. The cards were manufactured by Real Time Devices (State College, Penn.). The temperature sensors (model LM34CH, National Semiconductor, Santa Clara, Calif.) with a voltage output of 10 mV/EF built into the SOMMA were calibrated against thermistors certified to 0.01EC (PN CSP60BT103M, Thermometrics, Edison, N.J.) using a certified mercury thermometer as a secondary standard. These sensors monitored the temperature of SOMMA components, including the pipette, gas sample loops, and the coulometer cell. The SOMMA software was written in GWBASIC Version 3.20 (Microsoft Corp., Redmond, Wash.), and the instruments were driven from an options menu appearing on the PC monitor. With the coulometers operated in the counts mode, conversions and calculations were made using the SOMMA software rather than the programs and the constants hardwired into the coulometer circuitry.

The SOMMA-coulometry systems were calibrated with pure CO_2 using an eight-port gas sampling valve (GSV). The GSV had two sample loops of known volume determined gravimetrically by the method of Wilke et al. (1993). These two loops were connected to a source of pure CO_2 through an isolation valve with the vent side of the GSV plumbed to a barometer. When a gas loop was filled with CO_2, the mass (moles) of CO_2 contained therein was calculated by dividing the loop volume (V) by the molar volume of CO_2 at the ambient temperature (T) and pressure (P). The molar volume of CO_2 [$V(CO_2)$] was calculated from the gas constant (R), loop temperature (T), the instantaneous barometric pressure (P), and the first virial coefficient B(T) for pure CO_2:

$$V(CO_2) = RT / P \times [1+ B(T) / V(CO_2)] \ .$$

The ratio of the calculated mass to that determined coulometrically, known as the gas calibration factor (CALFAC), was used to correct the subsequent titrations for small departures from 100% recoveries (DOE, 1994). Pressure was measured with a barometer, model 216B-101 Digiquartz Transducer (Paroscientific, Inc., Redmond, Wash.) which was factory-calibrated for pressures between 11.5 and 16.0 psi. The standard operating procedure was to make three sequential gas calibrations for each newly born titration cell (normally, one cell per day) at a carbon age of between 3 and 6 mgC titrated.

The “to-deliver” volume (V_{cal}) of the sample pipettes was determined and calibrated gravimetrically prior to the cruise and periodically during the cruise by collecting aliquots of deionized water dispensed from the pipette into preweighed serum bottles. The serum bottles were crimp sealed and returned to shore, where they were reweighed on a model R300S balance (Sartorius, Goettingen, Germany). The apparent weight (g) of water collected (W_{air}) was corrected to the mass in vacuo (M_{vac}) from:

$$M_{vac} = W_{air} + W_{air} \, (0.0012 / \tilde{n} \ ! \ 0.0012 / 8.0) \ ,$$

where 0.0012 is the sea level density of air at 1 atm, ñ is the density of the calibration fluid at the pipette temperature and sample salinity, and 8.0 is the density of the stainless steel weights.

The “to-deliver” volume (V_{cal}) was calculated by dividing the mass in vacuo (M_{vac}) by the density of the calibration fluid at the pipette temperature and sample salinity (ñ), as illustrated:

$$V_{\mathrm{cal}} = M_{\mathrm{vac}} / \tilde{n}\ .$$

The V_{cal} of the pipette for the BNL discrete system (004) calculated from the pipette aliquots taken during the cruise and weighed post cruise was 20.8386 ± 0.0044 mL (n = 12, Rel. Std. Dev. = 0.02%) at a calibration temperature (t_{cal}) of 22.24EC. The precruise volume could not be used because the original pipette installed on the BNL system was broken during transit and had to be replaced with a new pipette that had not been calibrated prior to the cruise. The precruise volume for the IfMK discrete system (014) was 21.4371 mL at 14.66EC. These pipette volumes were used for the calculation of the sample TCO_2. During the A8 section, the mean temperature of the sample pipettes was 21.5 ± 1.26EC (n = 1588). The sample “to-deliver” volume (V_t) at the measured pipette temperature was calculated from the expression:

$$V_t = V_{\mathrm{cal}}\ [1 + a_v\ (t - t_{\mathrm{cal}})]\ ,$$

where a_v is the coefficient of volumetric expansion for Pyrex-type glass (1×10^{-5} / EC), and t is the temperature of the pipette sample at the time of measurement.

The coulometers used to detect CO_2 were electronically calibrated as described in Johnson et al. (1993) and DOE (1994). Briefly, at least two levels of current (usually 50 and 2 mA) were passed through an independent and very precisely known resistance (R) for a fixed time. The voltage (V) across the resistance was continuously measured, and the instantaneous current (I) across the resistance was calculated from Ohm’s law and integrated over the calibration time. Then, the number of pulses (counts) accumulated by the VFC during this time was compared with the theoretical number computed from the factory-calibration of the VFC [frequency = 10^5 pulses (counts) generated per sec at 200 mA] and the measured current. If the VFC was perfectly calibrated at the factory, then the electronic calibration procedure would yield a straight line passing through the origin (intercept = 0 = INT_{ec}) with a slope ($SLOPE_{ec}$) of 1. The results for the precruise in-house electronic calibration and mean gas CALFAC for the coulometers on the Section A8 Cruise are given in Table 3. The BNL laboratory’s electronic calibrations showed that the factory-calibration for both coulometers was almost perfect. The CALFAC remained very stable over the duration of the cruise (Rel. St. Dev. = 0.05% corresponds to a 1 Fmol/kg change in sample TCO_2 concentration).

Table 3. The electronic calibration and the mean gas calibration coefficients for the coulometers used on WOCE Section A8

System	**$SLOPE_{ec}$**	**INT_{ec} (Fmol/min)**	**CALFAC (n)**	**S. D.**	**Rel. S. D. (%)**
004	1.000490	0.000740	1.004000 (19)	0.000520	0.05
014	1.000052	0.0000584	1.002816 (38)	0.000408	0.04

The factory-calibration of the VFC and the value of the Faraday (96489 Coulomb/mol) yielded a scaling factor of 4.82445 × 10^3 counts/Fmol. The theoretical mass (M) of carbon titrated (M, in Fmol) from water samples or the gas loops was calculated by (1) dividing the number of pulses or counts by the scaling factor, (2) subtracting the difference between the products of (a) the slope intercept (INT_{ec}) and the time in minutes during the titration where current flow was continuous (T_i) and (b) the system blank in Fmol per minute and the length of the titration in minutes; and then (3) dividing the resultant by the slope ($SLOPE_{ec}$). More simply stated:

$$M = [\text{Counts} / 4824.45\ !\ (\text{Blank} \times T_t)\ !\ (INT_{ec} \times T_i)] / SLOPE_{ec}\ .$$

Note that the slope obtained from the electronic calibration procedure applied for the entire length of the titration, but the intercept correction applied only for the period of continuous current flow (usually 3 to 4 min) because the electronic calibration procedure can only be carried out for periods of continuous current flow. For water samples, the TCO_2 concentration in Fmol/kg was calculated from:

$$TCO_2 = M \times CALFAC \times [\ 1 / (V_t \times ñ)] \times d_{Hg}$$

where ñ is the density of seawater in g/mL at the measurement temperature and sample salinity calculated from the equation of state given by Millero and Poisson (1981), and d_{Hg} is the correction for sample dilution with bichloride solution (for Section A8 d_{Hg} = 1.00066).

System 004 was equipped with a conductance cell (Model SBE-4, Sea-Bird Electronics, Inc., Bellevue, Wash.) for the determination of salinity as described by Johnson et al. (1993). SOMMA and CTD salinity were compared to ensure that the salinity of the analyzed samples matched the assigned salinity. The agreement between CTD and SOMMA salinity was 0.04 or better. However, all calculations of TCO_2 in the last expression are based on the WOCE sample salinity furnished by the chief scientist.

The first phase of the three-phase quality control-quality assurance (QC-QA) process was assessed through the accuracy of the 77 CRM analyzed on board the ship on WOCE Section A8. These data are summarized in Table 4 and their temporal distribution during Section A8 is plotted in Fig 3.

Table 4. Comparison of the at-sea mean analytical difference (ÄTCO_2 = measured ! certified) and the standard deviation of the differences between analyzed and certified TCO_2 on WOCE Section A8

System	No.[a] (*n*)	Mean (Fmol/kg)	S. D. (Fmol/kg)	ÄTCO_2 (Fmol/kg)	Outliers[b]
004	27	1992.23	0.92	0.29	0
014	50	1991.21	0.85	-0.73	1
All	77	1991.57	0.99	-0.37	1

[a] Batch 21 CRM with a certified TCO_2 of 1991.94 ± 0.76 Fmol/kg (*n* = 10) at S = 34.54.

[b] See text for description.

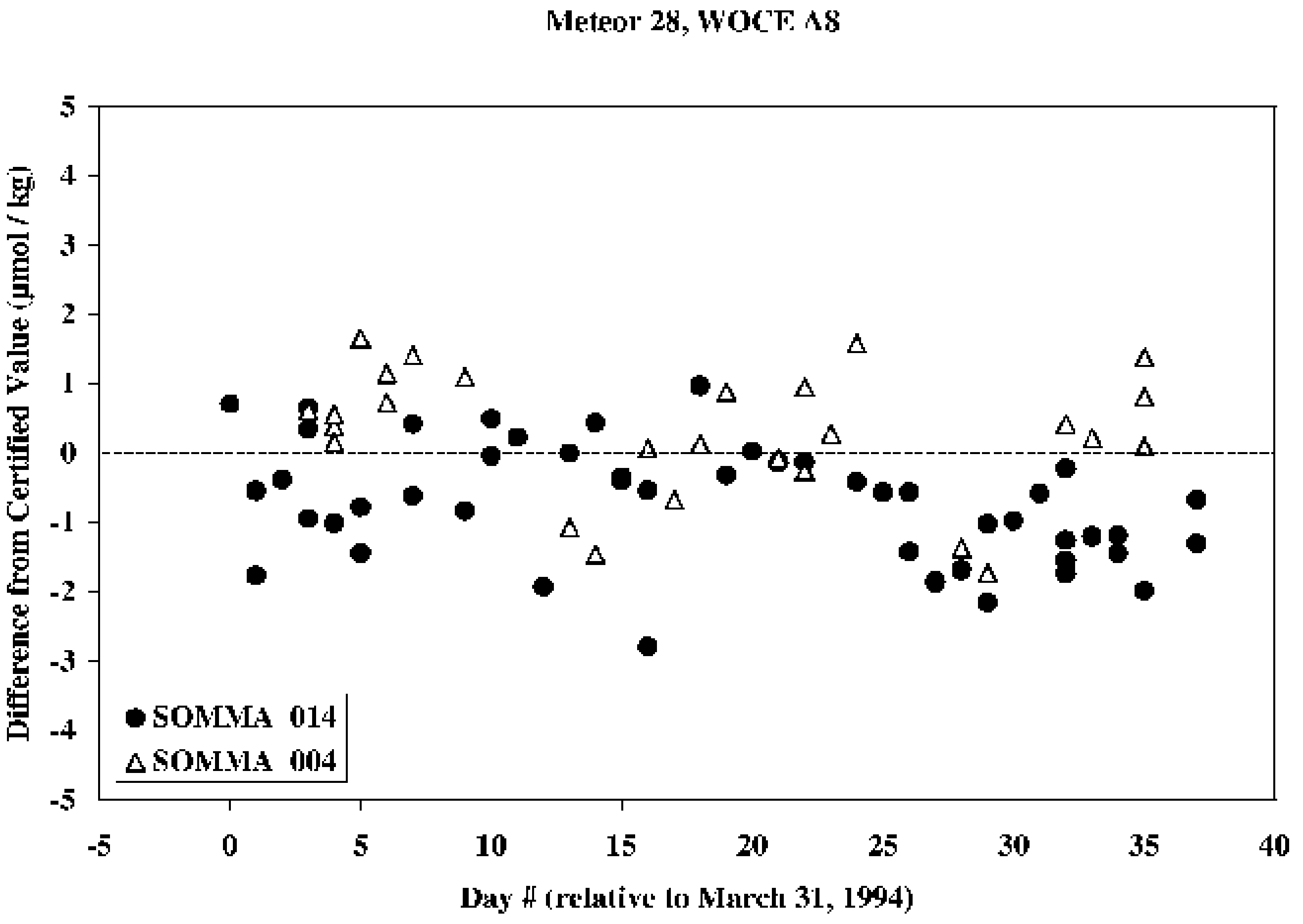

Fig. 3. The temporal distribution of differences between the measured and certified TCO_2 for CRM analyzed on SOMMA-coulometry systems 004 (open triangles) and 014 (closed circles) during WOCE Section A8. The differences were calculated by subtracting the certified TCO_2 from the measured TCO_2.

Only one CRM analysis was considered an outlier and was dropped from the data set. This occurred on April 4 on System 014 for CRM No. 42 at a carbon age of 29 mgC titrated. The analytical difference was !8 Fmol/kg. This might be explained as one of the compromised CRM (damaged seal) described earlier. After this result, CALFAC was redetermined, but it was not different than the factor originally determined at a carbon age of 6 mgC titrated. Hence there is no evidence for a change in system response as the cell prepared on 4 April aged. Although no visual damage was noted to the stopper seal of this bottle, this CRM exhibited an unusual amount of grease in and floating on the surface of the liquid phase, and it was suspected that it may have been compromised. However, no additional seawater samples were analyzed with this cell. Table 4 and Fig. 3 show that both systems gave very high accuracy throughout the A8 section with results virtually identical to the Certified TCO_2 with an overall precision of ± 0.99 Fmol/kg (n = 77), which also compares favorably with the precision (± 0.76 Fmol/kg; n = 10) of the bench mark vacuum extraction/manometric method. The response of both systems (Table 4) remained constant during the cruise.

The second phase of the QC-QA procedure was an assessment of precision that is presented in Table 5. The single-system precision was determined from samples with duplicates analyzed on the same system (either 004 or 014). The sample precision was calculated using duplicates that were analyzed on both systems (004 and 014).

Table 5. Precision of the discrete TCO_2 analyses on WOCE Section A8

Mean absolute difference						**Pooled standard deviation**			
F$_{bs}$	**S. D.**	**K**	**F$_{bn}$**	**S. D.**	**K**	**S_p^2 Fmol/kg**	**K**	**n**	**d.f.**
Fmol/kg			**Fmol/kg**						
Single-system precision									
0.92	1.01	198	0.77	1.07	49	1.03	208	488	280
Sample precision									
1.45	1.26	46	1.20	0.78	19	1.17	46	155	109

Single-system and sample precision have been separately assessed in Table 5 as:

- "between-sample" precision (ó$_{bs}$), which is the mean absolute difference between duplicates (*n* = 2) drawn from the same Niskin bottle;
- "between-Niskin" precision (ó$_{bn}$), which was the mean absolute difference between duplicates (*n* = 2) drawn from two different Niskin Bottles closed at the same depth;
- the pooled standard deviation (S_p^2), calculated according to Youden (1951) where K was the number of samples with duplicates analyzed, *n* was the total number of replicates analyzed from K samples, and *n* ! K was the degrees of freedom (d.f.).

Single-system precision provided a measure of drift in system response during a sequence of sample analyses. This is because the time elapsed between duplicate analyses on the same system using the same coulometer cell was deliberately kept at from 3 to 12 hours on the assumption that drift or change in response would be reflected in the single-system precision by an increase in the imprecision of the duplicate analyses. Sample precision, on the other hand, was measured because TCO$_2$ measurements were made on two separate systems and an estimate of overall sample precision for the section(s), independent of which analytical system was used, was required. Sample precision is the most conservative estimate of precision, incorporating several sources of random or systematic (bias) error.

As on other Sections in the North Atlantic (e.g. A10, A24, A20, A22) where SOMMA-coulometer systems have been run in parallel, the sample precision was slightly less precise than the single-system precision. Following established precedent for systems run in parallel the precision and accuracy of the TCO$_2$ determination on Section A8 was taken to be the pooled sample standard deviation (S_p^2) of ± 1.17 µmol/kg given in Table 5. These data, showing an equivalent high precision between systems 004 and 014 and good agreement between single-system and sample precision, indicate that changes in system response during the coulometer cell lifetime or system bias (see also Table 4) did not occur in either system during the cruise. The agreement between “between-sample” and “between-Niskin” precision indicates that there were no significant analytical effects due to gas exchange with the overlying headspace of the Niskin bottles during sampling. These findings were consistent with data from other cruises (Johnson et al., 1996; 1998). The precision and accuracy of the TCO$_2$ determination on Section A8 was ± 1.17 µmol/kg. These data probably represent the maximum performance to be expected for these systems under field conditions.

The final step in the QC-QA procedure was the ship-to-shore comparison. Here sample duplicates were analyzed in real time at sea by continuous gas extraction/coulometry and later, after storage, on shore by vacuum extraction/manometry. The manometric analyses were completed by February 1995 in the laboratory of C. D. Keeling at SIO for 16 samples collected at 10 Section A8 stations. The results of the comparison are given in Table 6. Tables 4, 5, and 6 and Fig. 3 show an internally consistent TCO$_2$ data set for the A8 section with excellent accuracy, consistently good precision, no significant analytical bias between the systems, and excellent agreement between the at-sea and shore analyses. Hence no correction for instrumental bias or CRM differences has been applied to the data, and the TCO$_2$ data clearly meet the survey criterion for accuracy and precision. Additionally, the data submitted have not been normalized to a salinity of 35. Figure 4 summarizes the analytical results as a contour-section plot of the TCO$_2$ data from the WOCE Section A8 in Atlantic Ocean along 11.3E S.

The mean ship-to-shore analytical difference (ÄTCO$_{2(SIO)}$, n = 16) was ! 1.62 ± 1.50 Fmol/kg, and the mean absolute difference was 1.92 Fmol/kg. The lower ship-based TCO$_2$ for Section A8 was consistent with previously reported results for A9, A1E, and A10 (Johnson et al. 1995, 1996, 1998) and for the program in general (Wallace 2002). The reason for ship-based TCO$_2$ being lower than the shore-based results is not known as of this time. While only three analyses shown in Table 6 were made on system 004, (ÄTCO$_{2(SIO)}$ = ! 0.66 Fmol/kg) and 13 were made on the IfMK system 014 (ÄTCO$_{2(SIO)}$ = ! 1.96 Fmol/kg), the difference between the two systems was consistent with the sample precision (± 1.17 Fmol/kg).

Table 6. Comparison of the at-sea analyses of TCO_2 by coulometry and the on-shore analyses of TCO_2 by manometry on aliquots of the same sample

Station	**Date**	**Niskin (No.)**	**Depth (m)**	**TCO_2 (at-sea) (Fmol/kg)**	**TCO_2 (SIO) (Fmol/kg)**	**Ä$TCO_{2(sea\text{-}SIO)}$ (Fmol/kg)**
232	21.04.94	324	12.9	2034.13(2)[a]	2035.26	! 1.13
232[b]	21.04.94	311	2500.0	2186.15	2186.05	+0.10
234[b]	22.04.94	324	10.8	2058.46	2056.96	+1.50
238	23.04.94	311	2849.1	2192.00(2)	2195.11	!3.11
244	25.04.94	324	9.2	2050.01(2)	2051.39	!1.38
244	25.04.94	311	3501.9	2205.30(2)	2208.57	!3.27
248	26.04.94	324	12.9	2058.02(2)	2059.47	!1.45
248	26.04.94	311	3758.5	2208.84(2)	2213.14	!4.30
250[b]	27.04.94	311	3852.5	2209.01(2)	2212.60	!3.59
256	29.04.94	324	13.0	2056.62(2)	2058.27	!1.65
260	01.05.94	324	11.5	2012.12(2)	2013.60	!1.48
260	01.05.94	311	3001.1	2199.53(2)	2200.24	!0.71
264	02.05.94	324	12.3	2039.73	2039.99	!0.26
264	02.05.94	311	996.9	2235.96(2)	2238.27	!2.31
268	03.05.94	324	1.0	2020.53(2)	2021.10	!0.57
268	03.05.94	311	1597.7	2191.11(2)	2193.38	!2.27
Mean						!1.62
S. D.						±1.50[c]
n						16

[a] The number 2 in parentheses means the TCO_2 is the mean of two analyses. The SIO results are always the mean of 2 analyses.

[b] Analyzed on System 004.

[c] The precision of the method was ± 1.17 Fmol/kg.

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Fig. 4. Distribution of the total CO_2 in seawater along WOCE Section A8. This figure was made by use of the Ocean Data View program (Schlitzer 2001).

3.3 Discrete *f*CO_2 Measurements

A total of 1549 individual samples were collected in 60-mL serum bottles for discrete *f*CO_2 analysis. The analysis and calculations followed the method of Neill et al. (1997). The serum bottles were crimp-sealed, a small amount of water was withdrawn from the bottle, leaving a liquid phase of ~54 mL and a gas phase of -6 mL. The introduced gas phase was a mixture of CO_2 in N_2 drawn from a gas-sampling bag and was therefore at atmospheric pressure. Three different concentrations of CO_2 in N_2 were used in order that the partial pressure difference between the liquid and gas phases was kept to a minimum. Normally, near-surface samples (0–250 m) were exposed to a gas phase close to the atmospheric partial pressure of CO_2 (~380 ppm), whereas samples collected from deeper water (> 250 m) were exposed to a gas phase with *f*CO_2 of ~750 ppm. Toward the eastern end of the section (station numbers > 244), very high *f*CO_2 values were measured at intermediate depths and a third headspace gas with *f*CO_2 of ~1450 ppm was used for samples from between ~200 m and 1000 m.

Following headspace introduction, the sealed serum bottles were shaken (equilibrated) for ~3 hours at constant temperature [temperature was held constant to < 0.05EC and was measured with a thermistor equipped with a National Institute of Standards and Technology (NIST)-traceable calibration to an accuracy of 0.005EC]. Most of the samples were equilibrated at ~20EC, however near-surface temperatures along the section were as high as 29EC. In order to maintain a positive pressure in the headspace of the serum bottle during equilibration, samples collected from water depths with a potential temperature > 20EC were equilibrated at sample temperatures of 30 to 32EC. For samples that were equilibrated at the higher temperatures, there was a risk that water vapor would condense in the connecting tubing or sample loop, effectively decreasing the volume of gas injected into the gas chromatograph. This was controlled for and checked by periodically equilibrating duplicate samples at both temperatures and comparing the results following normalization to the same temperature (see discussion of correction in the following paragraphs).

After equilibration, the headspace pressure was measured with a quartz crystal pressure transducer (Paroscientific Inc.; model 216B; 0-45 PSIA). The barometer was connected to a fixed, low-dead-volume side-port needle that was pointed downward and inserted through the septum cap of the serum bottle. The dead volume of the transducer-needle assembly in use with the system was determined to be 290 FL (compared with a nominal headspace volume of ~6 mL), and all headspace pressure data were corrected accordingly.

Following this pressure measurement, the headspace was displaced and flushed through a 0.45 mL sample loop. The mole fraction of CO_2 in the headspace gas was measured by injecting the contents of this loop (at known temperature and pressure) into a gas chromatograph (GC) equipped with a flame ionization detector (FID) and using catalytic conversion of CO_2 to CH_4. The GC measurements were calibrated against a set of four separate CO_2 in air standards (CO_2 mixing ratios of 265, 352, 743, and 1536 pptv) that had previously been intercalibrated with standards maintained in the laboratory of Taro Takahashi and David Chipman at the Lamont-Doherty Earth Observatory (D. Chipman, personal communications, 2001). A calibration curve based on these four standards was run at the beginning and end of the analysis of the samples from a station. In addition, a check standard (743 pptv) was run after the analysis of every four water samples.

The process of equilibrating the water samples with an introduced headspace involves repartitioning of CO_2 between the liquid and gas phases. This in turn alters the TCO_2 of the water sample and its *f*CO_2. The *f*CO_2 measured after equilibration is therefore perturbed from the *f*CO_2 that the sample would have had if no headspace had been introduced. This effect was corrected for using a mass balance for inorganic carbon based on separate TCO_2 measurements on (not equilibrated) duplicate samples using the SOMMA system and knowledge of the introduced headspace gas content. The correction was made using the apparent dissociation constants of CO_2 in seawater (Roy et al. 1993) and the constraint that the total alkalinity of the water sample remained unchanged during the equilibration. The motivation for the use of variable headspace gases (see earlier discussion) was to minimize the magnitude of these corrections by closely matching the $f\mathrm{CO}_2$ of the introduced headspace to that of the sample. The calculation procedure and associated errors are discussed in detail by Neill et al. (1997).

The mass-balance-corrected results are reported as $f\mathrm{CO}_2$ at both the actual temperature of equilibrium and also, for convenience, at a constant temperature of 20°C. The actual temperature of equilibration is also reported. The correction to 20°C was made using the program CO2SYS of Lewis and Wallace (1998) using the CO_2 solubility data of Weiss (1974) and the dissociation constants of Roy et al. (1993). Based on measurement of 93 duplicate samples, the precision of the $f\mathrm{CO}_2$ analysis was ~1%.

The samples that were equilibrated in the warmer equilibration bath (30 to 32°C) consistently showed a small positive offset after normalization to a common equilibration temperature when compared with the replicates that were equilibrated in the cooler bath. It was hypothesized that the offset was the result of water condensing out of the headspace gas as it passed through the headspace sampling needle and transfer tubing, thereby increasing the mole fraction of CO_2 within the gas that filled the sample loop that was injected into the gas chromatograph. A theoretical calculation, which assumed that the headspace gas was 100% saturated with $\mathrm{H_2O}$ at the equilibration temperature as it entered the needle and was 100% saturated at room temperature as it entered the heated sample loop housing, was in good agreement with the observed offset. A correction for this effect has therefore been applied to all samples that were equilibrated in the warmer bath. Following this cruise, the system was modified to include heated transfer tubing to prevent such condensation.

The partial pressure of CO_2 (pCO_2) data presented in this NDP was calculated by R. Key of Princeton University using the equations taken from Weiss 1974. Figure 5 summarizes the analytical results as a contour-section plot of the calculated pCO_2 data from the WOCE Section A8 in Atlantic Ocean along 11.3° S.

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Fig. 5. Distribution of the discrete pCO_2 in seawater along WOCE Section A8.
This figure was produced by the Ocean Data View program (Schlitzer 2001).

4. DATA CHECKS AND PROCESSING PERFORMED BY CDIAC

An important part of the numeric data packaging 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 data obtained during the R/V *Meteor* cruise 28/1 along WOCE Section A8 in the South Atlantic Ocean.

1. The final carbon-related data were provided to CDIAC by D. W. R. Wallace and K. M. Johnson of Brookhaven National Laboratory (BNL). 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 90 retrieval code was written and used to merge and reformat all data files.

2. To check for obvious outliers, all data were plotted by use of 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. 6 and 7). Several outliers were identified and marked with the quality flags of “3” (questionable measurement) or “4” (bad measurement) (see File Descriptions in Part 2 of this documentation).

3. To identify “noisy” data and possible systematic, methodological errors, property-property plots for all parameters were generated (Fig. 8), carefully examined, and compared with plots from previous expeditions in the South Atlantic Ocean.

4. All variables were checked for values exceeding physical limits, such as sampling depth values that are greater than the given bottom depths.

5. Dates, times, and coordinates were checked for bogus values (e.g., values of MONTH < 3 or > 5; DAY < 1 or > 31; YEAR < or > 1994; TIME < 0000 or > 2400; LATITUDE < 12ES or > 5E S; LONGITUDE < 40E W or > 15E E.

6. Station locations (latitudes and longitudes) and sampling times were examined for consistency with maps and cruise information supplied by D. W. R. Wallace and K. M. Johnson of BNL.

7. The designation for missing values, given as !9.0 in the original files, was changed to !999.9 for the consistency with other oceanographic data sets.

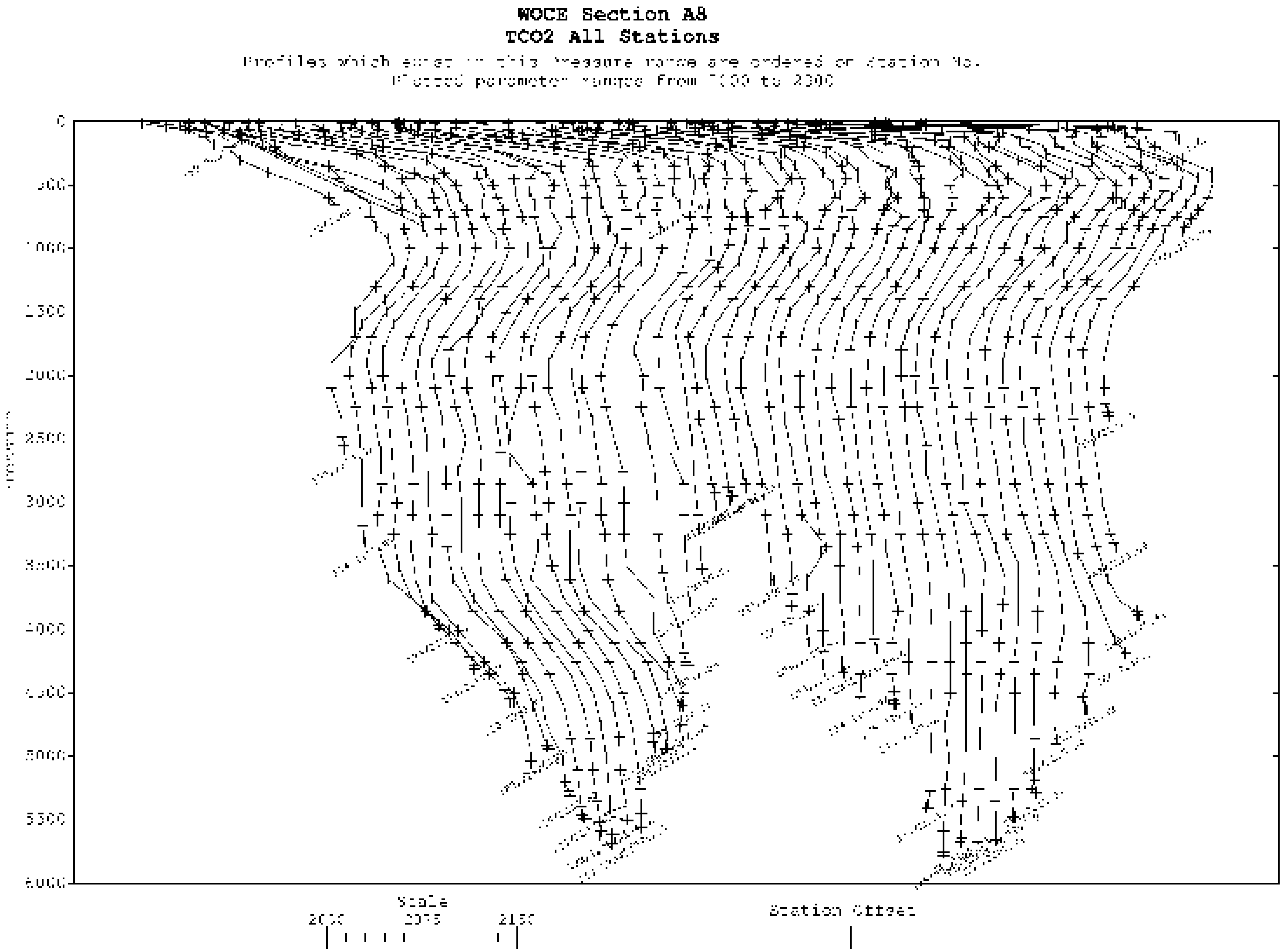

Fig. 6. Nested profiles: Total CO_2 (Fmol/kg) vs pressure (dbar) for all stations of WOCE Section A8.

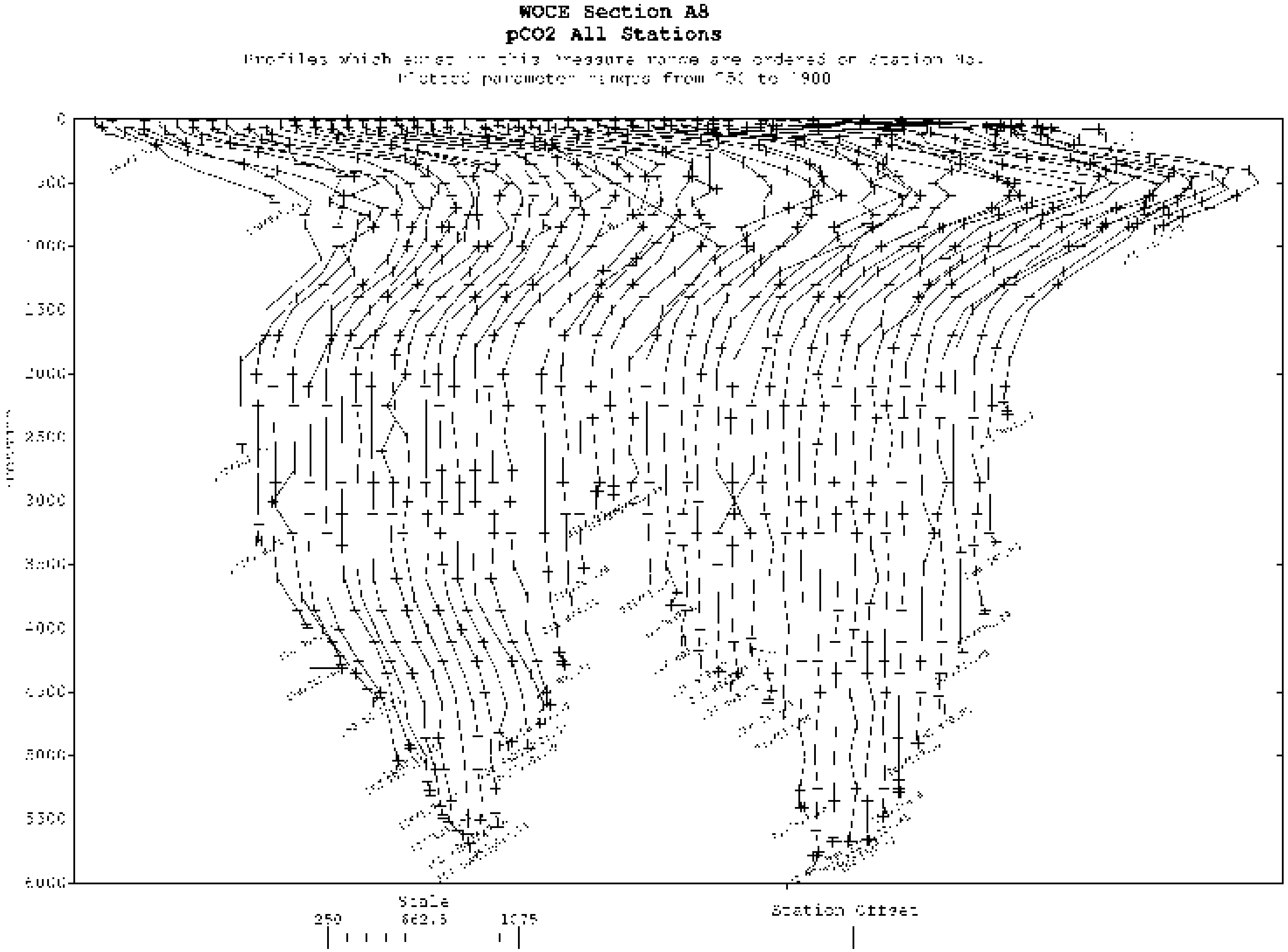

Fig. 7. Nested profiles: pCO_2 (μatm) vs pressure (dbar) for all stations of WOCE Section A8.

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Fig. 8. Property-property plots for all stations occupied during the R/V *Meteor* cruise along WOCE Section A8.

5. HOW TO OBTAIN THE DATA AND DOCUMENTATION

This database (NDP-079) is available free of charge from CDIAC. The complete documentation and data can be obtained from the CDIAC oceanographic Web site: http://cdiac.ornl.gov/oceans/doc.html), through CDIAC's online ordering system (http://cdiac.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 160.91.18.18
Login: “anonymous” or “ftp”
Password: your e-mail address
ftp> cd pub/ndp079/
ftp> dir
ftp> mget (files)
ftp> quit
```

Contact information:

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Internet: http://cdiac.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 7). Because CDIAC distributes the data set in several ways (via the Web, CDIAC's online ordering system, or anonymous FTP), each of the five files is referenced by both an ASCII file name, which is given in lower-case, bold-faced type (e.g., **ndp079.txt**), and a file number. The remainder of this section describes (or lists, where appropriate) the contents of each file.

Table 7. Content, size, and format of data files

File number, name, and description	Logical records	File size in bytes
1. **ndp079.txt**: a detailed description of the cruise network, the two FORTRAN 90 data-retrieval routines, and the two oceanographic data files	1,337	89,101
2. **stainv.for**: a FORTRAN 90 data-retrieval routine to read and print **a08sta.dat** (File 4)	44	1,340
3. **a08dat.for:** a FORTRAN 90 data-retrieval routine to read and print **a08.dat** (File 5)	57	2,232
4. **a08sta.dat**: a listing of the station locations, sampling dates, and sounding bottom depths for each station of the WOCE Section A8	249	18,849
5. **a08.dat:** hydrographic, carbon dioxide, and chemical data from all stations occupied on WOCE Section A8	3,853	650,464
Total	5,540	761,986

7.1 ndp079.txt (File 1)

This file contains a detailed description of the data set, the two FORTRAN 90 data-retrieval routines, and two oceanographic data files. It 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 90 data-retrieval routine to read and print **a08sta.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 **a08sta.dat** in Sect. 7.4.

```
c*********************************************************************
c* FORTRAN 90 data retrieval routine to read and print the files
c* named "a08sta.dat″ (File 4).
c*********************************************************************

       INTEGER  stat, cast, depth
       REAL latdcm, londcm
       CHARACTER expo*10, sect*3, date*10, time*4
       OPEN (unit=1, file='a08sta.dat')
       OPEN (unit=2, file='a08sta.data')
       write (2, 5)

 5     format (1X, 'STATION INVENTORY: R/V Meteor Cruise 28/1',/,
     1 1X,'EXPOCODE',3X,'SECT',1X,'STNBR',2X,'CAST',9X,
     2 'DATE',2X,'TIME',2X,'LATITUDE',2X,'LONGITUDE',2X,
     3 'DEPTH',/)

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

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

 10    format (A9, 4X, A3, 3X, I3, 5X, I1, 3X, A10, 2X, A4, 3X,
     1 F7.3, 3X, F8.3, 3X, I4)

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

 20    format (A9, 4X, A3, 3X, I3, 5X, I1, 3X, A10, 2X, A4, 3X,
     1 F7.3, 3X, F8.3, 3X, I4)

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

```
       end
```

7.3 a08dat.for (File 3)

This file contains a FORTRAN 90 data-retrieval routine to read and print **a08.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 **a08.dat** in Sect. 7.5.

```
c********************************************************************
c* FORTRAN 90 data retrieval routine to read and print the file
c* named “a08.dat” (File 5).
c********************************************************************

       CHARACTER qualt*11
       INTEGER sta, cast, samp, bot
       REAL pre, ctdtmp, ctdsal, theta, sal, oxy, silca, nitrat
       REAL cfc11, cfc12, tcarb, fco2eq, eqtmp, fco2, pco2
       OPEN (unit=1, file='a08.dat')
       OPEN (unit=2, file='a08.data')
       write (2, 5)

 5     format (2X,'STNNBR',2X,'CASTNO',2X,'SAMPNO',2X,'BTLNBR',2X,
     1 'CTDPRS',2X,'CTDTMP',2X,'CTDSAL',3X,'THETA',4X,'SALNTY',2X,
     2 'OXYGEN',2X,'SILCAT',1X,'NO2+NO3',3X,'CFC-11',3X,'CFC-12',
     3 2X,'TCARBN',4X,'FCO2',3X,'EQTMP',4X,'FCO2',4X,'PCO2',7X,
     4 'QUALT',/,
     5 36X,'DBAR',2X,'ITS-90',2X,'PSS-78',2X,'ITS-90',4X,'PSS-78',
     6 1X,3('UMOL/KG',1X),1X,'PMOL/KG',2X,'PMOL/KG',1X,'UMOL/KG',
     7 2X,'PPM@EQ',3X,'DEG_C',1X,'PPM@20C',1X,'UAT@20C',11X,'*',/,
     8 25X,'*******',17X,'*******',11X,4('*******',1X),1X,'*******',
     7 2X,3('*******',1X),16X, '*******',11X,'*')

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

 7     CONTINUE
       read (1, 10, end=999) sta, cast, samp, bot, pre, ctdtmp,
     1 ctdsal, theta, sal, oxy, silca, nitrat, cfc11, cfc12,
     2 tcarb, fco2eq, eqtmp, fco2, pco2, qualt

 10    format (5X, I3, 5X, I3, 4X, I4, 5X, I3, 1X, F7.1, 1X, F7.4,
     1 1X, F7.4, 1X, F7.4, 1X, F9.4, 1X, F7.1, 1X, F7.2, 1X, F7.2,
     2 1X, F8.3, 1X, F8.3,1X, F7.2, 1X, F7.2, 1X, F7.1, 1X, F7.2,
     3 1X, F7.2, 1X, A11)
```

```
      write (2, 20) sta, cast, samp, bot, pre, ctdtmp,
    1 ctdsal, theta, sal, oxy, silca, nitrat, cfc11, cfc12,
    2 tcarb, fco2eq, eqtmp, fco2, pco2, qualt

20    format (5X, I3, 5X, I3, 4X, I4, 5X, I3, 1X, F7.1, 1X, F7.4,
    1 1X, F7.4, 1X, F7.4, 1X, F9.4, 1X, F7.1, 1X, F7.2, 1X, F7.2,
    2 1X, F8.3, 1X, F8.3,1X, F7.2, 1X, F7.2, 1X, F7.1, 1X, F7.2,
    3 1X, F7.2, 1X, A11)
      GOTO 7
999   close(unit=1)
      close(unit=2)
      stop
      end
```

7.4 a08sta.dat (File 4)

This file provides station inventory information for each station occupied during the R/V *Meteor* cruise along WOCE Section A8. Each line of the file contains an expocode, section number, station number, cast number, sampling date (month/date/year), sampling time, latitude, longitude, and sounding depth. The file is sorted by station number and can be read by using the following FORTRAN 90 code (contained in **stainv.for**, File 2):

```
       INTEGER stat, cast, depth
       CHARACTER expo*9, sect*3, date*10, time*4
       REAL latdcm, londcm

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

 10    format (A9, 4X, A3, 3X, I3, 5X, I1, 3X, A10, 2X, A4, 3X,
     1 F7.3, 3X, F8.3, 3X, I4)
```

Stated in tabular form, the contents include the following:

Variable	Variable type	Variable width	Starting column	Ending column
expo	Character	9	1	9
sect	Character	3	14	16
stat	Numeric	3	20	22
cast	Numeric	1	28	28
date	Character	10	32	41
time	Character	4	44	47
latdcm	Numeric	7	51	57
londcm	Numeric	8	61	68
depth	Numeric	4	72	75

The variables are defined as follows:

expo	is the 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 a08.dat (File 5)

This file provides hydrographic, carbon dioxide, and chemical data for all stations occupied during the R/V *Meteor* cruise along WOCE Section A8. Each line consists of a station number, cast number, sample number, bottle number, CTD pressure, CTD temperature, CTD salinity, potential temperature, bottle salinity, bottle oxygen, silicate, nitrate-plus-nitrite, CFC-11, CFC-12, TCO$_2$, *f*CO$_2$ @ equilibrator temperature, equilibrator temperature, *f*CO$_2$ @ 20EC, calculated pCO$_2$ @ 20EC, and data-quality flags. The file is sorted by station number and pressure and can be read by using the following FORTRAN 90 code (contained in **a08dat.for,** File 3):

```
        CHARACTER qualt*11
        INTEGER sta, cast, samp, bot
        REAL pre, ctdtmp, ctdsal, theta, sal, oxy, silca, nitrat
        REAL cfc11, cfc12, tcarb, fco2eq, eqtmp, fco2, pco2

        read (1, 10, end=999) sta, cast, samp, bot, pre, ctdtmp,
      1 ctdsal, theta, sal, oxy, silca, nitrat, cfc11, cfc12,
      2 tcarb, fco2eq, eqtmp, fco2, pco2, qualt

 10     format (5X, I3, 5X, I3, 4X, I4, 5X, I3, 1X, F7.1, 1X, F7.4,
      1 1X, F7.4, 1X, F7.4, 1X, F9.4, 1X, F7.1, 1X, F7.2, 1X, F7.2,
      2 1X, F8.3, 1X, F8.3,1X, F7.2, 1X, F7.2, 1X, F7.1, 1X, F7.2,
      3 1X, F7.2, 1X, A11)
```

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	3	14	16
samp	Numeric	4	21	24
bot	Numeric	3	30	32
pre	Numeric	7	34	40
ctdtmp	Numeric	7	42	48
ctdsal	Numeric	7	50	56
theta	Numeric	7	58	64
sal	Numeric	9	66	74
oxy	Numeric	7	76	82
silca	Numeric	7	84	90
nitrat	Numeric	7	92	98
cfc11	Numeric	8	100	107
cfc12	Numeric	8	109	116
tcarb	Numeric	7	118	124
fco2eq	Numeric	7	126	132
eqtmp	Numeric	7	134	140
fco2	Numeric	7	142	148

pco2	Numeric	7	150	156
qualt	Character	9	158	168

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)];
theta	is the potential temperature (°C);
sal[a]	is the bottle salinity (on the PSS);
oxy[a]	is the oxygen concentration (Fmol/kg);
silca[a]	is the silicate concentration (Fmol/kg);
nitrat[a]	is the nitrate-plus-nitrite concentration (Fmol/kg);
cfc11[a]	is the chlorofluorocarbon 11 (pmol/kg);
cfc12[a]	is the chlorofluorocarbon 12 (pmol/kg);
tcarb[a]	is the total carbon dioxide concentration (Fmol/kg);
fco2eq[a]	is the fugacity of CO_2 @ equilibrator temperature (ppm);
eqtmp	is the temperature of equilibration of the $f\text{CO}_2$ samples in equilibrator (EC);
fco2	is the fugacity of CO_2 @ 20EC (ppm);
pco2[a]	is the calculated partial pressure of CO_2 @ 20EC (Fatm);
qualt	is a 14-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.