CARBON DIOXIDE, HYDROGRAPHIC, AND CHEMICAL DATA OBTAINED DURING THE R/V *KNORR* CRUISES 138-3, -4, AND -5 IN THE SOUTH PACIFIC OCEAN (WOCE SECTIONS P6E, P6C, AND P6W, MAY 2 – JULY 30, 1992)

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ACRONYMS

ADCP	acoustic Doppler current profiler
BOD	biological oxygen demand
BNL	Brookhaven National Laboratory
^{14}C	radiocarbon
CALFAC	calibration factor
CDIAC	Carbon Dioxide Information Analysis Center
CFC	chlorofluorocarbon
CO_2	carbon dioxide
CTD	conductivity, temperature, and depth sensor
CSIRO	Commonwealth Scientific and Industrial Research Organisation
CRM	certified reference material
CUV	Catholic University Valparaiso
DOE	U.S. Department of Energy
FTP	file transfer protocol
GC	gas chromatograph
GLODAP	Global Ocean Data Analysis Project
GMT	Greenwich mean time
GSV	gas sampling valve
IAPSO	International Association for the Physical Sciences of the Ocean
JGOFS	Joint Global Ocean Flux Study
LDEO	Lamont-Doherty Earth Observatory
nm	nautical mile
NDP	numeric data package
NOAA	National Oceanic and Atmospheric Administration
ODF	Ocean Data Facility
ONR	Office of Naval Research
OSU	Oregon State University
pCO_2	partial pressure of CO_2
PMEL	Pacific Marine Environmental Laboratory
PSS	Practical Salinity Scale
PU	Princeton University
QA	quality assurance
QC	quality control
R/V	research vessel
RSMAS	Rosenstiel School of Marine and Atmospheric Sciences
SIO	Scripps Institution of Oceanography
SOMMA	Single-Operator Multiparameter Metabolic Analyzer
TALK	total alkalinity
TCO_2	total carbon dioxide
UW	University of Washington
VFC	voltage to frequency converter
WHOI	Woods Hole Oceanographic Institution
WHPO	WOCE Hydrographic Program Office
WOCE	World Ocean Circulation Experiment
WHP	WOCE Hydrographic Program

ABSTRACT

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This data documentation discusses the procedures and methods used to measure total carbon dioxide (TCO_2) and partial pressure of carbon dioxide (pCO_2) at hydrographic stations during the research vessel (R/V) *Knorr* oceanographic cruises 138-3, -4, and -5 in the South Pacific Ocean (Section P6). The work was divided into three legs designated as P6E, P6C, and P6W which correspond to cruises 138-3, -4, and -5, respectively. Conducted as part of the World Ocean Circulation Experiment (WOCE), the P6 section began in Valparaiso, Chile, on May 2, 1992, and ended 81 days later in Sydney, Australia, on July 30, 1992. Measurements made along WOCE Section P6 included pressure, temperature, salinity [measured by a conductivity, temperature, and depth sensor (CTD)], bottle salinity, bottle oxygen, silicate, nitrate, nitrite, phosphate, radiocarbon (^{14}C), TCO_2, and pCO_2.

TCO_2 was measured coulometrically by use of two Single-Operator Multiparameter Metabolic Analyzers (SOMMAs). The precision and accuracy of the measurements was ±1.65 µmol/kg. The pCO_2 in discrete samples was measured using a headspace-equilibration technique and gas chromatography with precision of ~1 to 2%. The CO_2-related measurements aboard the R/V *Knorr* were supported by the U.S. Department of Energy.

The P6 data set is available free of charge as a numeric data package (NDP) from the Carbon Dioxide Information Analysis Center. The NDP consists of three oceanographic data files, three station inventory 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 instructions for accessing the data.

Keywords: carbon dioxide; TCO_2; pCO_2; coulometry; gas chromatography; World Ocean Circulation Experiment; Pacific Ocean; hydrographic measurements; 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 obtain a better understanding of the ocean's role in climate and climatic changes resulting from both natural and anthropogenic causes. The need for this experiment arose from the 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 unevenly distributed because of poorly characterized and 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 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. Goals 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 carbonate system parameters TCO_2 and the partial pressure of CO_2 (pCO_2) measured aboard the research vessel (R/V) *Knorr* on the three legs comprising WOCE Zonal Section P6. The section began in Valparaiso, Chile, on May 2, and ended in Sydney, Australia, on July 20, 1992 (Fig. 1), with stops at Easter Island, Chile, and Auckland, New Zealand. The P6 Section was divided into three legs (P6E, P6C, and P6W) and scientists from Brookhaven National Laboratory (BNL) were responsible for the carbonate system measurements on all of these legs. The Chief Scientists, scientific crew, and CO_2 measurement groups from BNL were exchanged after each leg. Based on the measurements from these sections and the data from other Pacific sections occupied during the WOCE Survey (Lamb et al. 2001), the large-scale three-dimensional distribution of temperature, salinity, and chemical constituents including the carbonate system parameters will be mapped. Knowledge of these parameters and their initial conditions will allow determination of heat and water transports as well as carbon transport. An understanding of these transports will contribute to the understanding of processes that are relevant for climate change.

2. DESCRIPTION OF THE EXPEDITION

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

The R/V *Knorr*, built in 1969 by the Defoe Shipbuilding Company in Bay City, Michigan, is owned by the U.S. Navy. It was turned over to the Woods Hole Oceanographic Institution in 1971 for operation under a charter agreement with the Office of Naval Research (ONR). It was named for E. R. Knorr, a hydrographic engineer and cartographer who in 1860 held the title of Senior Civilian and Chief Engineer Cartographer of the U.S. Navy Office. Its original length and beam were 245 and 46 feet, respectively. Beginning on February 6, 1989, it underwent a major mid-life retrofit or "jumbo-izing" at the McDermott Shipyard in Amelia, Louisiana. A midsection was added to the ship to stretch its length by 34 feet to 279 feet, and fore and aft azimuthing propulsion systems were added to make it one of the most maneuverable and stable ships in the oceanographic fleet while on station. By the time it was returned to the Woods Hole Oceanographic Institution in late 1991, the retrofit had consumed 32 months. The P6 Section was the first scientific cruise after the retrofitting. The R/V *Knorr* was designed for a wide range of oceanographic operations, possesses anti-roll tanks and an ice strengthened bow, and like its sister ship, the R/V *Melville*, it is used for ocean research and routinely carries scientists from many different countries. Table 1 provides a list of technical characteristics of the R/V *Knorr*, while Table 2 provides individual cruise information, parameter measured, institution, and responsible personnel.

Table 1. Technical Characteristics of the R/V *Knorr*

Ship name: R/V *Knorr*

Call Sign: KCEJ

Basic Dimensions:

Gross registered tonnage	2518 T	Displacement	2958 lT
Overall length	279 ft	Beam	46 ft
Draught (maximum)	16.5 ft	Service speed	12 kn
Maximum speed	14.5 kn	Minimum speed	0.1 kn
Main Deck Clear length	126 ft		

Personnel   Crew: 24
                         Scientists: 34

Main engine $4 \rightarrow \times$ Mak6M 322 = 4 × 1000 kW at 750 rpm

Propulsion   Twin Lips diesel-electric, azimuthing stern thrusters, 1500 SHP

Bow thruster   Lips retractable azimuthing 900 SHP

Fuel capacity   160,500 gallons

Maximum cruise duration   60 days (12,000 nm)

Nautical equipment :   Integrated navigation system
                Potable water generator
                2 instrument hangars
                Winches: 1 heavy duty trawl with 30,000 ft of ½ inch wire
                        2 hydrographic, both with 30,000 ft of hydrowire
                Hydraulic cranes on the starboard side aft and midships
                Scientific storage space of 1,320 ft^2
                Portable van space
                Machine shop
                Fume hoods
                Uninterruptable power supply
                Air conditioning
                Library/lounge,
                3680 ft^2 of laboratory space for multidisciplinary research

Table 2. R/V *Knorr* Cruise Information, Parameter Measured, Institution, and Responsible
Personnel

R/V *Knorr*	Cruise number		
	138-3 (Leg P6E)	138-4 (Leg P6C)	138-5 (Leg P6W)
Ports of call	Valparaiso, Chile Easter Island, Chile	Easter Island, Chile Auckland, New Zealand	Auckland, New Zealand Sydney, Australia
Dates	May 2–May 26	May 30–July 7	July 13–July 31
Chief Scientist	Dr. H. Bryden, WHOI	Dr. M. McCartney, WHOI	Dr. J. M. Toole, WHOI
Parameter	Responsible personnel		
ADCP[1]	M. Kosro, OSU	M. Kosro, OSU S. Pierce, OSU	M. Kosro, OSU S. Pierce, OSU
Chilean Observer	S. Marchant, CUV		
Chlorofluorocarbons (CFCs)	R. Weiss, SIO K. Sullivan, RSMAS	R. Weiss, SIO F. Van Woy, SIO	R. Weiss, SIO F. Van Woy, SIO
CTD[2], salinity	H. Bryden, WHOI M. Schwartz, WHOI	M. McCartney, WHOI M. Schwartz, WHOI	J. Toole, WHOI
Nutrients	L. Gordon, OSU A. Ross, OSU H. Garcia, OSU	L. Gordon, OSU J. Jennings, OSU	L. Gordon, OSU J. Jennings, OSU
Oxygen	G. Knapp, WHOI	M.Stalcup, WHOI	G. Knapp, WHOI
PCO$_2$	C. Neill, BNL K. Johnson, BNL	M. Haines, BNL R. Wilke, BNL	V. Coles, BNL K. Johnson, BNL
Radiocarbon (^{14}C)	R. Key, PU R. Rotter, PU	R. Key, PU G. McDonald, PU	R. Key, PU G. McDonald, PU
TCO$_2$	K. Johnson, BNL K. Wills, BNL	R. Wilke, BNL D. Hunter, BNL	K. Johnson, BNL B. Tilbrook, CSIRO
Tritium, ^{3}He	B. Jenkins, WHOI M. Mathewson, WHOI	B. Jenkins, WHOI S. Birdwhistell, WHOI	B. Jenkins, WHOI M. Mathewson, WHOI
Underway pCO$_2$	R. Weiss, SIO	R. Weiss, SIO	R. Weiss, SIO

Participating institutions: Brookhaven National Laboratory, Upton, NY (BNL); Commowealth Scientific and Industrial Research Organisation, Australia (CSIRO); Catholic University, Valparaiso, Chile (CUV); Oregon State University, Corvallis, OR (OSU); Princeton University, Princeton, NJ (PU); Rosensteil School of Marine and Atmospheric Science, University of Miami, Miami, FL (RSMAS); Scripps Institution of Oceanography, University of California, San Diego, CA (SIO); University of Washington, Seattle, WA (UW); and Woods Hole Oceanographic Institution, Woods Hole, MA (WHOI).

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

2.2 Brief Cruise Summary

The P6 Section really began in mid-April 1992 in Jacksonville, Florida, when BNL personnel (K. M. Johnson, R. Ramirez, and R. Wilke) placed two Single-Operator Multiparameter Metabolic Analyzers (SOMMA, S/Ns 004 and 006) and a gas chromatograph (GC) system for measuring discrete pCO$_2$ aboard the R/V *Knorr*. The ship was berthed in Jacksonville for the final adjustments following its first shake-down cruise after refitting. The BNL CO$_2$ group trucked its scientific gear to Jacksonville to save the cost and trouble of shipping it to Chile. Preliminary operational tests of the measurement systems were made, customs declarations filled out, and the instruments were secured for transit to Valparaiso before the BNL group departed ship. The equipment placed on board the ship in Jacksonville was used for the entire P6 Section so that subsequent staging was minimal.

The BNL CO_2 group, consisting of K. M. Johnson, C. Neill, and K. Wills, departed New York on April 28, 1992, and arrived in Santiago, Chile, on the 29th. Upon arrival to the pier, the R/V *Knorr* was docking, and the group boarded the ship almost immediately and began the testing of the SOMMA and pCO_2 GC systems placed aboard in Jacksonville. A number of problems developed during the testing phase. The SOMMAs were plagued with contamination and noise from unknown sources. Trouble-shooting was interrupted temporarily while the CO_2 group moved aboard the ship on May 1, 1992, and the P6E Leg began with the departure of the ship from Valparaiso at 0900 on May 2 under the command of Captain Carl Swanson with Harry Bryden as Chief Scientist.

Trouble-shooting and repair continued, and two serious problems with the SOMMA systems were determined. The first finding was that very brief electrical surges were spontaneously causing the 8-port gas sample valve used in the gas calibration procedure to attempt to switch from the "load" to the "inject" position. The surges were not powerful enough to cause the valve to actually switch or cause the operator to hear the valve trying to switch, but they were strong enough to enable "cross talk" between the valve ports. Cross-talk momentarily connects the calibration gas, in this case pure CO_2, to the carrier gas line, and the unwanted sporadic introduction of CO_2 into the analytical stream interfered with sample titrations. This was only discovered after three very frustrating days by resting the palm of the hand on the gas sample valve chassis. In this way the silent and spontaneous surges could be felt through the metal valve cover. This problem was corrected by placing an uninterruptable power supply (UPS) in-line and by unplugging the gas sample valve from the mains when it was not needed. This left a second problem—a much smaller, steadier, but still unsatisfactory source of noise manifesting itself as an unacceptably high blank. This noise resulted because the carrier gas cylinders of N_2 were stored in a hangar external to the laboratory containing the SOMMA systems. Futhermore, thermoplastic lines (in some cases as long as 50 feet) were used to connect the cylinders to the SOMMA systems. These lines apparently allowed enough air (containing CO_2) to diffuse through the tubing walls, thus interfering with the sample titrations. This problem was corrected by relocating the cylinders within the laboratory to within 6 to 10 feet of the SOMMAs. This relocation along with the installation of the normal CO_2 scrubbers in the carrier gas lines reduced the blank to satisfactory levels. The pCO_2 system also got off to a rocky start resulting from some initial software problems that required some code to be rewritten.

The first WOCE CTD station on P6E was station No. 4 with a depth of only 100 m at 32° 30' S and 71° 30' W. Stations 1 through 3 were not included in Section P6E so that there were 69 WOCE CTD stations on this leg. A CO_2 group collected samples at 34 of the 69 stations (~ 50%) (see Fig. 2).

Some 1,043 individual water samples along with 98 duplicates and 92 certified reference material (CRM) were analyzed for TCO_2. The pCO_2 was determined on 323 of these samples. Because of initial set-up problems, the pCO_2 sampling could not begin until
Station 23.

As the analytical work proceeded during P6E, the members of the CO_2 group became aware of an additional problem with one of the SOMMA systems (S/N 004). In this case, the recovery of the CO_2 calibration gas during the gas calibration procedure was approximately 0.2% lower than expected based on prior experience with these systems (99.4 vs 99.6%). This lower recovery was associated with an analytical difference between the measured and CRM TCO_2 of +3 to −4 µmol/kg (measured amount minus certified amount). This suggested that the gas-calibration was in error, and the relief measurement group was asked to bring a spare gas sample valve with them to Easter Island for installation at the conclusion of the P6E Leg.

The ship's operations following the retrofit were not without incident. In addition to the power surges mentioned, at least 2 complete power black-outs were experienced, the ship vibrated strongly, and there was noticeable buckling of specific deck plates. The vibration was of particular concern because of the possibility of damage to the computer hard disks. With the exception of the power outages, these problems did not cause any instrumental downtime. A lack of fuel availability on Easter Island required conservation measures such as lower ship speeds for the P6 Legs.

The P6E Leg ended with the anchoring of the R/V *Knorr* at 0800 on May 26, 1992, off the village of Hanga Roa on Easter Island. The first measurement group went ashore after lunch and obtained accommodations. The second measurement group consisting of R. Wilke, D. Hunter, and M. Haines came aboard as the first group left. They carried with them some badly needed replacement parts including a gas sample valve, a refrigerated bath, silver electrodes, and fittings. Change-over between the groups took place on May 28 and 29, and the equipment was ready when the ship pulled anchor and departed on Leg P6C on May 30, 1992, with Mike McCartney as the Chief Scientist.

The second leg, P6C, which crossed the Southwest Pacific Basins and occupied stations from the East Pacific Rise ridge crest to the Kermadec Islands, began with Station 73 which was a reoccupation of the last station of the P6E Leg (72). Both Stations 73 and 74 are co-located with Station 72. The leg continued along 32° 30' S from 112° 40' W until 178° 55' E, the location of Station 184. Thereafter P6C angled northward and ended with Station 188 at 31° 05' S and 177° 32' E. During this leg, additional duplicate stations were made such that Station 141 was co-located with 142 and 187 with 188. The CTD results from station 112 are unreliable because of the failure of the CTD. Of the 113 CTD stations occupied during P6C, 109 are unique WOCE stations. The CO_2 group collected samples at 51 of the 109 stations (Fig.3) or 47%. 1739 samples along with 157 duplicates and 162 CRM were analyzed for TCO_2. Discrete measurements of pCO_2 were made on 314 of these samples.

With respect to the TCO_2 systems, the gas sample valve for system 004 was replaced before the start of section P6C. However, the recovery of the CO_2 calibration gas did not improve, and it remained constant and slightly low (99.4%) as on the first Leg P6E. No additional repairs were attempted. Otherwise sampling and analysis for the carbonate system parameters remained routine. Unfortunately, of the three legs comprising the P6 Section the P6C measurement group experienced the worst weather, and it was the longest of the three legs. The pCO_2 system experienced numerous problems indicated by a loss of precision as this leg went on. Modifications were made in coordination with the shore-based BNL measurement group members, but precision continued to decline such that the last station run on P6C was Station 125 on June 19, 1992. In addition to poor precision, other problems reported included component temperature changes as a result of lack of sufficient insulation and traffic through the area where GC was located, exhaustion of the H_2 generator's silica gel scrubber, unprogrammed gas sample valve switching in the GC (further evidence of electrical problems), dirty valve rotors, very rough weather that made trouble-shooting very difficult, and finally a thorough cleaning of the GC hardware on June 26 that resulted in the loss of all response upon restart. Daily efforts were made to bring the system back and response was gradually restored. It was not until the *Knorr* docked in Auckland and replacement parts brought by the relief crew were installed that the system was restored to function for the last Leg (P6W). Hence, pCO_2 was not determined between Stations 126 and 190. The P6C station work concluded on July 4, and the R/V *Knorr* arrived at Auckland on July 7.

The relief crew from BNL, consisting of K. M. Johnson and V. Coles, were joined in Auckland by Bronte Tilbrook from the CSIRO Division of Oceanography located in Tasmania, Australia. Change-over and coordination between the relieved and relief groups occurred between July 7 and July 9. Complaints from several sources about the electric power on board ship on both Legs P6E and P6C lead to the acquisition and installation of a harmonic filter for the ship's "clean power" supply. Repairs were also made to one of the CTD winches. The ship departed from Auckland to take on fuel for the third and final Leg (P6W) at 0900 on July 13, 1992, with John Toole as Chief Scientist and Carl Swanson as Master. At 1600, following fueling, the R/V *Knorr* headed north and picked up where P6C left off with Station 189 which is co-located with Stations 188, 187, and 190. It continued northward to 30° 05' S and 176° 30' E. From 176° 30' E the cruise continued along 30° 05' S to the Australian coast finishing with Station 246 at 153° 29' E. This station was followed by several additional CTD calibration stations (247–267) which are not considered or included in the WOCE data sets.

During P6W, additional duplicate casts were made such that Station 233 is co-located with 234, Station 246 with 247, and Stations 237 through 246 are co-located with Stations 248 through 257 and 258 through 267, so that of the 78 CTD stations occupied during P6W, only 55 represent unique WOCE stations. The CO_2 group collected samples at 22 of these 55 stations (40%) (Fig. 4), and 502 water samples along with 47 duplicates and 41 CRM were analyzed for TCO_2. Discrete measurements of pCO_2 were made on 171 of these samples beginning with station 191. On this leg only one SOMMA (S/N 006) was used. The station work concluded on July 29, and the R/V *Knorr* arrived in Sydney on July 30, 1992 after uniformly good working conditions.

As on previous cruises, not all stations could be sampled for TCO_2 and pCO_2 parameters because of the time required to analyze the samples from each station. With 46% of the P6 stations sampled and profiled for TCO_2, the goal of 50% coverage was essentially achieved. The coverage for pCO_2 was considerably less (25%). The standard WOCE parameters (temperature, oxygen, nutrients, and salinity) were analyzed on all samples, and the carbonate system samples were normally drawn in conjunction with the tracer samples which included He, ^{14}C, and the CFCs. Sampling frequency was at least every 30 nautical miles, but shorter intervals as a function of bathymetry—shallow waters or changing depths required more stations—were common, especially on P6W. A minimum vertical depth resolution was maintained at 200 m throughout the P6 section. Table 3 presents a summary of the carbonate system measurements made on the WOCE section P6.

Table 3. The number of stations sampled for carbonate system parameters (CSP) and the number of CSP determinations on WOCE Section P6

Leg	Stations			Number of CSP Determinations			
	CTD	CSP	%	Discrete	Duplicate	CRM	Total
TCO_2 Measurements							
P6E	68	34	50	1043	98	92	1233
P6C	109	51	47	1739	157	162	2058
P6W	55	22	40	502	47	41	590
Totals	232[a]	107	46	3284	302	295	3881
pCO_2 Measurements							
P6E	68	21	31	323	27	0	350
P6C	109	22	20	314	73	0	387
P6W	55	16	29	171	35	0	206
Totals	232[a]	59	25	808	135	0	943

[a]Excludes duplicate and test CTD stations. On the P6C Leg one station (112) was thrown out because of a CTD malfunction so severe that the data could not be recovered.

3. DESCRIPTION OF VARIABLES AND METHODS

3.1 Hydrographic Measurements

Position and depth were manually logged every 10 minutes on the P6 Section. A thermosalinograph (Falmouth Scientific Instruments) was mounted on the bow ~ 3 m below the surface and operated on all legs except the latter stages of Leg P6C. An underway fluorometer was operated on Legs P6E and P6C, until it also failed toward the end of Leg P6C and was not used again. Water samples were collected using a 36-position underwater frame and 10-L sample bottles designed and constructed by the Ocean Data Facility (ODF) at SIO. Modified Neil Brown MkIII CTD instruments mounted on the 36-bottle frame were used for data acquisition. The CTD (Nos. 7, 9, and 10) were supplied by the WHOI Group with No. 10 being used for the bulk of the

work. CTDs 7 and 9 were used only very sparingly on Leg P6C when CTD 10 required electronic repairs. On the other legs their use was largely restricted to test stations. Small shifts between the pre- and post-cruise pressure and temperature CTD calibrations were found, but the P6 CTD data have been corrected according to procedures given by Millard et al. (1992), and the CTD salinity data have been empirically corrected to conform to the bottle salinity. The prescribed WOCE sample order was as follows: CFCs, helium, oxygen, CO_2, nutrients, tritium, and salinity. Surface currents were measured continually during the cruise with a hull-mounted ADCP, and current profiles were also made during the CTD casts with an ADCP mounted on the rosette frame.

Some problems were experienced with the CTD/rosette systems. The CTD oxygen sensor functioned poorly on Leg P6E particularly in the top several 100 m probably because of cavitation of a specially installed pump used to circulate water past the sensor. This pump was not used on Legs P6C or P6W. Problems with the data acquisition software were noted and corrected on Leg P6E. CTD No. 10 failed on Leg P6C at Station 75, and CTD No 9. was used through Stations 76–85 while CTD 10 was repaired. Careful post-cruise verifications using the complete bottle data sets have been carried out, and the sample pressures and salinity assigned for each sample are to our knowledge correct.

Bottle salinity was measured on every water sample using 2 Guildline Autosal Model 8400A salinometers. The instruments (No. 10 and 11) were furnished by WHOI. The measurements were made in a climate-controlled portable laboratory secured to the deck of the ship. The temperature of the laboratory was kept at $22 \pm 1°C$. Salinity samples were the last water samples drawn from the rosette. The bottles and caps were rinsed twice and filled to ½ inch of the neck to leave an air space for expansion. The samples were thermally equilibrated in the laboratory before measurement (5–6 h). The salinometers were standardized with International Association for the Physical Sciences of the Ocean (IAPSO) Standard Sea Water (Batch P116), and a description of the salinity measurement is given by Knapp et al. (1990). Salinometer 11 was used until June 18 when it began to give intermittently higher results during the standardization. From this point on salinometer 10 was used. The precision of the salinity determination was the mean difference between duplicate salinity samples. For samples taken at less than and greater than 3000 m the precision was 0.0012 ($n = 107$) and 0.0011 ($n = 23$), respectively.

Bottle oxygen was measured on 50-mL aliquots of all P6 water samples by a modified Winkler titration technique (Knapp et al. 1990) using a computer-controlled titrator with amperometric end-point detection in a constant-temperature laboratory. Oxygen bottles were rinsed twice with sample water and carefully filled to overflowing to avoid air bubbles. Next the reagents were added (1 mL each of the $MnCl_2$ and NaI-NaOH), and the bottles shaken. Following thermal equilibration they were titrated with 0.01 sodium thiosulphate. The precision of the oxygen determination calculated from the mean difference and the standard deviation of the mean difference for 121 pairs of duplicate oxygen samples was ± 0.70 to ± 0.87 µmol/kg ($n = 98$) for depths <3000 m and ± 0.52 to ± 0.39 µmol/kg ($n = 23$) for depths >3000 m.

Phosphate, nitrate, nitrite, and silicate were determined on every bottle drawn from Stations 3 through 257. The nutrient concentrations were determined on samples collected in high-density polyethylene 30-mL tubes that were directly transferred to an autoanalyzer (AlpKem, Model 300 Rapid Flow Analyzer) according to procedures given by anonymous (1985) and Gordon et al. (1992; 1994). Samples were transferred to a climate-controlled laboratory and were analyzed within a few hours of collection. Standards and reagents were provided by the OSU group, and working standards (i.e., solutions having nitrate, nitrite, phosphate, and silica concentrations similar to those of the Pacific deep and bottom waters) were prepared from stock solutions every 4 to 7 days. Standard and stock solutions were kept refrigerated. Precision was measured by the difference between duplicate samples taken from the same rosette bottle analyzed one after the other (not separated in time) or at the start and end of the run (separated in time). Together the differences between replicate analyses is the short-term precision, which includes short-term

instrumental drift as well as random error. The mean standard deviations or short-term precision for the replicate analyses made on the three P6 Legs are: silicic acid ±0.16 to ±0.035 µmol/L; nitrite/nitrate ±0.05 to ±0.01 µmol/L phosphate ±0.011 to ±0.006 µmol/L. Long-term precision was estimated by comparing "old" working standard solutions made on the previous station with freshly made working standards (i.e., "new" standard solutions made for the current station). The long-term precision for the three P6 Legs are: silicic acid ±0.21 to ±0.028 µmol/L ($n = 284$); nitrate ± 0.087 to ±0.019 µmol/L ($n = 284$); phosphate ±0.015 to ±0.0006 µmol/L (n = 241); and nitrate ± 0.015 to
± 0.007 µmol/L ($n = 284$).

Problems with the nutrient analyses included nonlinearity for the nitrate/nitrite on Leg P6E through Station 112 on Leg P6C at which time a plumbing error was discovered and corrected. Post-cruise corrections have been applied to the nitrate/nitrite data through Station 112. In addition, the phosphate analysis was lost from Stations 171 through 188 on Leg P6C when noise rendered the phosphate channel unusable. This was corrected in Auckland prior to Leg P6W when the air injection phasing board was replaced.

3.2 Total Carbon Dioxide Measurements

TCO_2 was determined using two automated dynamic headspace sample processors (SOMMAs) 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 earlier publications (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 (450°C for 24 h) glass standard Biological Oxygen Demand (BOD) bottles, poisoned with 200-uL of a 50% saturated solution of $HgCl_2$, and analyzed for TCO_2 within 24 hours of collection (DOE Hand Book of Methods, 1994). Before analysis, they were stored in a refrigerator in darkness at ~15°C 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 the above conditions. CRMs were routinely analyzed according to DOE prescribed methods (1994). The CRMs were supplied by Dr. Andrew Dickson of the SIO, and during Section P6 batches 10 and 11 were used. The certified values for batch 10 were S = 34.5722 and Certified TCO_2 = 1960.67 ± 0.39 µmol/kg (n = 5). The corresponding numbers for batch 11 were S = 38.5 and TCO_2 = 2188.77 ± 0.56 µmol/kg (n = 5). The CRM TCO_2 concentration was determined by Vacuum-Extraction/Manometry in the laboratory of C. D. Keeling at SIO.

Seawater introduced from an automated "to-deliver" pipette into a stripping chamber was acidified, and the resultant CO_2 from continuous gas extraction was dried and coulometrically titrated on a model 5011 UIC Coulometer with a maximum titration current of 50 mA in the counts mode [the number of pulses or counts generated by the Coulometer's voltage to frequency converter (VFC) during the titration was displayed]. In the coulometer cell, the acid (hydroxyethylcarbamic acid) formed from the reaction of CO_2 and ethanolamine was titrated coulometrically (electrolytic generation of OH^-) with photometric endpoint detection. The product of the time and the current passed through the cell during the 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 was logged from its birth (time that electrical current is applied to the cell) until its death (time when the current is turned off). The age was measured in minutes from birth (chronological age) and in mgC titrated since birth (carbon age).

Each system was controlled with an IBM-compatible personal computer equipped with two

RS232 serial ports (coulometer and barometer), a 24-line digital Input/Output (I/O) card (solid state relays and valves), and an Analog to Digital (A/D) card (temperature, conductivity, and pressure sensors). The A/D cards were manufactured by Real Time Devices (State College, Pa.). The temperature sensors (model LM34CH, National Semiconductor, Santa Clara, Calif.), with a voltage output of 10 mV/°F built into the SOMMA were calibrated against thermistors certified to 0.01°C (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, the 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. Since 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 "to-deliver" volumes (V_{cal}) of the sample pipettes were determined (calibrated) gravimetrically prior to the cruise and were checked 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 weighed immediately during the on-shore laboratory calibrations, or were returned to shore and reweighed on a model R300S (Sartorius, Göttingen, Germany) balance as soon as possible. The apparent weight (g) of water collected (W_{air}) was corrected to the mass in vacuo (M_{vac}) from

$$M_{vac} = W_{air} + W_{air} \, (0.0012 \, / \, d - 0.0012 \, / \, 8.0) \, ,$$

where 0.0012 is the sea level density of air at 1 atm, d 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 was

$$V_{cal} = M_{vac} \, / \, d \, .$$

The calibration volumes (V_{cal}) at the calibration temperature (t_{cal}) of the SOMMA System pipettes for the the three P6 Sections are given in Table 4.

Table 4. The "to-deliver" pipette volume (V_{cal}) and calibration temperature (t_{cal}) for the SOMMA-Coulometer systems used on WOCE Section P6

Leg	System[a]	V_{cal} (mL)	St. Dev. (mL)	n	t_{cal} (°C)
P6E	004	25.5192	0.0069	6	14.93
P6C	004	25.5195	0.0059	8	15.62
P6E	006	29.6813	0.0000	2	15.83
P6C	006	29.6768	0.0045	17	14.86
P6W	006	29.6668	0.0030	8	14.87

[a]Note that system 004 was not used during the third Leg P6W.

The sample volume (V_t) at the pipette temperature was calculated from the expression

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

where a_v is the coefficient of volumetric expansion for Pyrex-type glass (1×10^{-5}/°C) and t is the temperature of the pipette at the time of a measurement. Table 4 shows a small decrease in V_{cal} for system 006 over time. This is consistent with other systems used daily for periods exceeding 30 days (Johnson et al. 1998a). The mean pipette temperature (t) during the P6 cruise was 15.12 ± 0.41°C ($n = 3580$).

The Coulometers used to detect CO_2 were periodically electronically calibrated as described in Johnson et al, (1993, 1996) and DOE (1994) throughout the P6 Section. For the calibration, 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 second at 200 mA] and the measured current. If the VFC was perfectly calibrated at the factory, the electronic calibration procedure would yield a straight line passing through the origin with an intercept (Int_{ec}) of 0 and a slope ($Slope_{ec}$) of 1. The factory-calibration of the VFC and the value of the Faraday (96489 Coulomb/mol) yields a scaling factor of 4.82445×10^3 counts/µmol, and the theoretical number of micromoles of carbon titrated (M) after extraction from water samples or the gas loops was

$$M = [Counts / 4824.45 - (Blank \times T_t) - (Int_{ec} \times T_i)] / Slope_{ec} ,$$

where T_t was the length of the titration in minutes, *Blank* is the system blank in µmol/min, Int_{ec} the intercept in µmol/min, and T_i the time in minutes during the titration where current flow was continuous. 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 can only be carried out for periods of continuous current flow. The results of the electronic calibrations are given in Table 5.

Table 5. Electronic calibration coefficients for SOMMA-Coulometer systems 004 and 006 on WOCE Section P6

Leg	System	Slope$_{ec}$	Int$_{ec}$ μmol/min	Period
P6E	004	1.000587	−0.000049	May 2–May 7
P6E	004	1.000524	0.000394	May 8–May 18
P6E	004	0.999905	0.000372	May 19–May 22
P6E,C	004	0.999708	0.000745	May 23–June 5
P6C	004	0.999693	0.001237	June 6–June 17
P6C	004	0.999733	0.001298	June 18–July 6
P6E	006	0.999567	0.000164	May 2–May 9
P6E	006	0.999673	0.000017	May 10–May 22
P6E	006	0.999589	0.000170	May 23–May 30
P6C	006	0.999708	0.000823	May 31–June 5
P6C	006	0.999716	0.001146	June 6–June 12
P6C	006	0.999554	0.001439	June 13–June 28
P6C	006	0.999638	0.001564	June 29–July 14
P6W	006	0.999659	0.000339	July 15–July 30

The SOMMA-Coulometry systems were also calibrated with pure CO_2 (calibration gas) using hardware consisting of an 8-port gas sampling valve (GSV) with two sample loops of known volume (determined gravimetrically by the method of Wilke et al. 1993) connected to the calibration gas 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 iteratively from T, P, and the first viral coefficient B(T) for pure CO_2:

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

The gas calibration factor (CALFAC)—the ratio of the calculated mass to that determined coulometrically—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.) that is factory-calibrated for pressures between 11.5 and 16.0 psia. The standard operating procedure was to make gas calibrations daily for each newly prepared titration cell [normally, one cell per day and three sequential calibrations per cell at a carbon age of 3 to 6 mgC with the result of the third calibration taken as the CALFAC if consistent with the second (i.e., agreement to ± 0.1% or better)]. The CALFAC data for the P6 section are summarized in Table 6.

Table 6. The mean gas calibration factors (CALFAC) obtained during the WOCE Section P6

Leg	Cells (n)	CALFAC Mean ± S.D.	Carbon Age Mean ± S. D. (MgC)

System 004 (CRM-based calibration)			
P6E	21	1.004037 ± 0.000777	10.1 ± 9.3
P6C	21	1.003932 ± 0.000538	10.9 ± 8.3
System 006 (pure-CO₂ calibration)			
P6E	24	1.004632 ± 0.000555	5.4 ± 1.6
P6C	30	1.004535 ± 0.000988	8.5 ± 3.2
P6W	18	1.004129 ± 0.000755	6.7 ± 1.8

For water samples, the TCO_2 concentration in µmol/kg was calculated from

$$TCO_2 \ = \ M \times CALFAC \times (1 \ / \ (V_t \times \rho)) \times d_{Hg} \ ,$$

where ρ 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 P6 d_{Hg} = 1.00066).

As noted above, the daily CALFAC determined for System 004 on the P6E Leg was too high (indicating lower recovery of CO_2), and when substituted into the last equation it led to over-estimates of the CRM TCO_2 concentration by 3 to 4 µmol/kg ($\geq 0.1\%$). Unfortunately, the cause of this problem was not discovered until a later cruise aboard the R/V *Meteor* (WOCE Section A10) in early 1993 when a leaky plumbing fitting was found and replaced on System 004 as described by Johnson et al. (1998b). For convenience, the line carrying the calibration gas (CO_2) to the GSV had been plumbed (prior to the P6 Section) with a tee connection on the upstream side of the GSV with one branch connected to the GSV through an isolation valve (IV) and the other branch to a Quick-Connect Fitting (Swagelok, Crawford Fitting). This plumbing configuration facilitated the rapid connection of the calibration gas to an external flow-meter and flow rate adjustments, however, the quick-connect fitting apparently allowed a very small of amount of air to infiltrate into the calibration gas line slightly diluting the calibration gas. The Quick-Connect and tee fittings were replaced early on the A10 Section and System 004 was successfully gas-calibrated thereafter.

For the P6E and P6C Legs, a "CRM-based calibration factor" was also calculated for System 004 by taking the resulting counts for the first CRM analyzed on each cell and substituting it along with the certified TCO_2 into the last equation and solving it for CALFAC. At the end of each leg, a leg-specific mean CRM-based CALFAC was calculated for System 004, and these data along with the mean CALFAC determined for System 006 are also given in Table 6. The TCO_2 measurements from sample analyses made on SOMMA 004 were calculated using the mean CRM-based CALFAC shown in Table 7, while TCO_2 on SOMMA 006 was calculated using the CALFAC determined daily using pure-CO_2 gas for each new cell born according to DOE (1994). Taken together, Tables 4 ("to-deliver" pipette volume), 5 (electronic calibration), and 6 (gas or CRM system (see Table 4).

The SOMMA 006 was equipped with a conductance cell (Model SBE-4, Sea-Bird Electronics, Inc., Bellevue, Wash.) for the determination of a salinity measurement as described by Johnson et al. (1993). Whenever possible SOMMA and CTD salinity were compared to ensure that the salinity of the analyzed samples matched the CTD salinity. The agreement between CTD and SOMMA salinity was 0.04 or better, and several mistrips of the Niskin bottles were quickly identified using this comparison.

Quality Control-Quality Assurance (QC-QA) was assessed from the results of 293 CRM analyses made on Systems 004 and 006. The mean differences between the measured and

certified TCO_2 (measured amount minus certified amount) were calculated for each leg, and the mean differences are summarized in Table 7. The individual differences for the Section P6 are plotted in Fig. 5.

Table 7. The mean analytical difference (ΔTCO_2 = measured − certified) and the standard deviation of the differences between measured and certified TCO_2 on WOCE Section P6

Leg	System	CRM (Batch)	ΔTCO_2 (μmol/kg)	St. Dev. (μmol/kg)	n
P6E	004	10, 11	−0.37	1.37	48
P6C	004	10, 11	+0.04	1.72	86
Total/Mean			−0.11	1.61	134
P6E	006	10, 11	+0.52	1.35	43
P6C	006	10, 11	−0.43	1.43	75
P6W	006	10, 11	−0.54	1.06	41
Total/Mean			−0.20	1.39	159
Overall/Total/Mean			−0.16	1.49	293

The accuracy of the CRM analyses was much better than 1 µmol/kg on both systems throughout the P6 Section, and the overall mean difference is −0.16 µmol/kg ($n = 293$). The precision of the CRM determination on the P6 Section is the standard deviation of the difference between determined and certified TCO_2 (±1.49 µmol/kg). The imprecision of the CRM analyses was slightly higher on the P6C Section for both systems, whereas the best precision was obtained on the final Leg P6W on System 006. There were two CRM analyses during Section P6 that were considered to be outliers, and these results have not been included in Table 7 or Fig. 5. An outlier was defined as an analytical difference between the measured and Certified TCO_2 which exceeds ±5.0 µmol/kg. The two outliers were measured on System 006: CRM No. 171 on June 6 at a carbon age of 38.8 mgC; and CRM No. 170 on June 21 at an age of 8.6 mgC. Additional CRMs were analyzed on both cells to within 1 µmol/kg of the certified TCO_2 even at very advanced carbon ages (55.5 and 46.1 mgC, respectively). Hence, the cause of the outlier values was likely not the behavior of the coulometric titration or cell, but may have been related to a temporary problem with the sample delivery system (pipette). Alternatively, the CRM may have been compromised during preparation or storage. Sample duplication with these cells was observed to be excellent, and accordingly the data obtained with them has been included in the data set described herein.

The second phase of the QC-QA procedure was the assessment of sample precision on each system (single-system precision) and the assignment of an overall precision to the P6 TCO_2 samples. This was the second cruise where two independent SOMMA systems were deployed side-by-side, and the conventions employed for the estimation of precision given for WOCE Sections A1E and A10 data (Johnson et al. 1996; 1998b) have been retained in Table 8.

Table 8. Summary of sample precision for TCO_2 analyses made during WOCE Section P6.

System	Mean Absolute Difference						The Pooled Standard Deviation			
	σ_{bs}	S. D. µmol/kg	K	σ_{bn}	S. D. µmol/kg	K	S_p^2 µmol/kg	K	n	d.f.
Single-System Precision										
004	0.94	0.84	73	0.83	1.19	8	0.89	86	186	100
006	0.73	0.66	194	0.53	0.53	28	0.71	198	398	202
All	0.78	0.72	267	0.61	0.71	36	0.76	284	586	302
Sample Precision										
P6	1.90	1.58	24				1.65	37	74	37

The single-system precision was determined from samples with duplicates analyzed on the same system (either 004 or 006). The sample precision was calculated using duplicates that were analyzed on both systems (004 and 006).

Single-system and sample precision have been separately assessed in Table 8 as:

- "between-sample" precision (σ_{bs}) which is the mean absolute difference between duplicates ($n = 2$) drawn from the same Niskin bottle;
- "between-Niskin" precision (σ_{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 provides 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 between 3 and 12 hours. Any temporal drift in system response would therefore be reflected in the single-system precision by decreased precision of the duplicate analyses. Sample precision, on the other hand, provides an estimate of overall sample precision for the section(s) independent of which analytical system was used. It was estimated because TCO_2 data were measured using two separate systems during the cruise. Sample precision is the most conservative estimate of precision, incorporating several sources of random or systematic (bias) error including errors associated with the inability to gas calibrate System 004.

It should be noted that the sample precision calculation includes the results for some samples (K = 13) that were analyzed in triplicate (i.e., two replicates analyzed on one system and the third on the second system). For these cases, the mean of the two replicate analyses was used for calculating S_p^2. Averaging the replicate results reduced the degrees of freedom term by making $n = 1$ for each system no matter how many replicates were actually run on each system. Without averaging (d.f. = 50), S_p^2 was ±1.50 μmol/kg, whereas with averaging (Table 8, d.f. = 37) S_p^2 increased to ±1.65 μmol/kg. For the P6 Section, the more conservative estimate of ±1.65 μmol/kg was chosen as the precision of the TCO_2 determination. This was in excellent agreement with the precision of the CRM determination (±1.49 μmol/kg).

As with other sections completed by the BNL measurement group using SOMMA-Coulometer systems run in parallel, the sample precision was slightly less precise than the single-system precision (1.65 μmol/kg vs <1.0, respectively). This indicates that any error introduced from changes in system response (drift) during the coulometer cell lifetime were within the overall precision of the method. The excellent agreement between "between-sample" and "between-Niskin" precision suggests that there were no significant analytical effects caused by the gas exchange with the overlying headspace of the Niskin bottles during the on-deck sampling. This is consistent with the data collected during other cruises (Johnson et al. 1996; 1998b). The P6 sample precision (±1.65 μmol/kg) was also in good agreement with the sample precision for the BNL WOCE Sections A1E (±1.65 μmol/kg), A10 (±1.92 μmol/kg), A8 (±1.17 μmol/kg), and the North Atlantic sections (±1.59 μmol/kg).

The difference between sample and single-system precision may be the result, in part, of the inability to perform daily gas-calibrations on System 004 during P6. Use of a single average CALFAC for an entire leg may, for example, have masked real cell-to-cell variations in CALFAC. This would have the effect of increasing imprecision but not necessarily altering overall accuracy (the positive and negative differences would cancel) as is suggested by Table 9. Table 9 provides additional proof of the overall accuracy and the absence of a bias between the two systems. Each system yields, within statistical precision, the same result for the same samples even though one system (006) was gas-calibrated daily and the other (004) was not (see also Tables 6, 7, and 8). Table 6 shows that the two calibration procedures gave stable and nearly identical results during the entire P6 Section. However, analyzing independent water sample duplicates on each system is the definitive test for accuracy, precision, and the calibration

procedures used. The accuracy of System 004 was validated in this way. This is similar to the situation previously described for the A10 Section (Johnson et al. 1998b) where only one of the two systems used possessed a gas-calibration unit and the gas-calibrated system served as the reference system.

Table 9. The mean TCO_2 and the mean analytical difference ($TCO_2 = 006 - 004$) for TCO_2 from CRM and water samples analyzed on both systems (004 and 006) during WOCE Section P6

Comparison	Mean		
	System 004 TCO_2 μmol/kg (n)	System 006 TCO_2 μmol/kg (n)	ΔTCO_2 (006 − 004) μmol/kg
CRM (Batch 10)	1960.63 (59)	1960.24 (73)	−0.39
CRM (Batch 11)	2188.76 (75)	2188.84 (85)	+0.08
Water samples	2171.58 (37)	2170.97 (37)	−0.61

The final step in the QC-QA procedure was the ship-to-shore comparison. Here sample duplicates (commonly called the "Keeling Samples") were analyzed "in real time" at sea by continuous gas extraction/coulometry and later, after shipment and storage, on-shore by vacuum extraction/manometry at the laboratory of C. D. Keeling at SIO (Guenther et al. 1994). The "Keeling Samples" were collected in specially provided threaded 500-mL glass bottles with 4 mL of headspace volume, poisoned with 100 μL of a saturated $HgCl_2$ solution, and then sealed air-tight with a greased ground glass stopper that was secured to the bottle with a threaded plastic screw cap. The latter was bored out to fit over the top of the stopper and mated to the bottle threads so that an air-tight seal was made by gently tightening the cap until a secure seal between the stopper and bottle was achieved. This procedure was carried out with 21 samples collected at 15 stations during P6. The results of the comparison are given in Table 10.

The mean ship-to-shore analytical difference was −2.64 μmol/kg ($n = 21$). The lower ship-based results for P6 are consistent with the ship-to-shore comparisons from Sections A9, A1E, and A10 previously reported (Johnson et al. 1995; 1996; 1998b). This negative bias for water samples was greater than the sample precision and the analytical difference observed for the CRM analyses (Wallace 2001). The reason for the tendency of the ship-based results to be lower than the shore-based results is not known at this time.

In aggregate, Tables 7–10 show an internally consistent data set with excellent accuracy, high single-system precision (<±1.0 μmol/kg), and a slightly higher imprecision for the sample precision (±1.65 μmol/kg). Based on Tables 7–10 and following the precedent of previous data submissions no correction for instrumental bias or CRM analytical differences has been applied to the sample data. Fig. 6 summarizes the analytical results as a contour section plot of the TCO_2 data from the WOCE Section P6 along 32.5° S.

Table 10. Comparison of the shipboard analyses of TCO$_2$ by coulometry and the shore-based reference analyses by manometry on duplicate samples.
The manometric analyses were completed by February of 1995 in the laboratory of
C.D. Keeling at SIO

Station	Date	Niskin	Depth (m)	TCO$_2$ (P6) (µmol/kg)	TCO$_2$ (SIO) (µmol/kg)	ΔTCO$_2$ (P6−SIO) (µmol/kg)
32	5/12	5	3006.9	2300.19	2302.70	−2.51
42[a]	5/15	8	3002.2	2294.39	2301.94	−7.55
46	5/16	36	18.6	2022.48	2023.65	−1.17
58	5/20	36	5.4	2016.23	2018.44	−2.21
58	5/20	5	3002.1	2294.45	2294.34	+0.11
68	5/23	36	12.2	2014.30	2014.72	−0.42
68	5/23	1	2771.9	2298.66	2302.19	−3.53
85	6/04	36	20.3	2010.10 (2)[b]	2014.15	−4.05
98[a]	6/08	36	19.2	2015.00 (2)	2017.40	−2.40
98[a]	6/08	7	2998.1	2298.90	2301.49	−2.59
123	6/18	35	61.3	2025.20	2027.79	−2.59
123	6/18	12	3117.9	2305.70	2310.94	−5.24
144	6/24	35	61.3	2033.70	2036.34	−2.64
144[a]	6/24	12	3007.5	2313.10	2316.60	−3.50
170	7/01	15	3041.2	2288.80	2290.42	−1.62
184	7/04	23	44.5	2045.50 (2)	2049.16	−3.66
188	7/05	31	3029.0	2309.80	2311.48	−1.68
231	7/22	24	20.2	2005.20 (2)	2009.57	−4.37
231	7/22	2	3135.3	2269.00	2272.61	−3.61
233	7/23	10	3001.6	2266.90	2268.49	−1.59
237	7/24	10	3004.6	2269.30	2267.89	+1.41
Mean						−2.64
S. D.						1.92
n						21

[a]Analyzed on System 004.
[b]Indicates TCO$_2$ is the mean of 2 analyses (the SIO TCO$_2$ values are always the mean of 2 analyses).

3.3 Discrete pCO$_2$ Measurements

Samples for discrete pCO$_2$ analyses were collected by overfilling 60-mL precalibrated serum bottles in the same manner as for oxygen and TCO$_2$. During Section P6 and following the static-

headspace procedure of Johnson et al. (1990) for CH_4, a plastic pipette tip was inserted into the bottles making a water-tight seal at the bottle mouth. Then the bottles were inverted so that the volume of water displaced into the pipette was decanted. Next, the pipette was quickly withdrawn and the bottles were crimp-sealed leaving a headspace (gas phase) volume in each bottle of (nominally) 5 mL and a liquid phase of (nominally) 55 mL, constituting a closed or static system. The pipette method yields a highly reproducible headspace volume, and the headspace and water volume for each (numbered) serum bottle was determined gravimetrically prior to the cruise. The bottles were prepared and sealed outside on deck at the CTD site usually within 1 minute of collection. The atmospheric pressure was measured just prior to sealing so that the pre-equilibrated serum-bottle gas phase contained air at a known mixing ratio of CO_2 (determined regularly throughout the cruise) at a known total pressure (P). The initial liquid phase temperature was taken to be the potential temperature (T) of the sample. The bottles were laid in a thermostatted shaking water bath and equilibrated, by shaking, for 3 h at 20°C. After equilibration, the serum-bottle gas phase was displaced by a brine solution to flush and fill a gas sample loop whose contents were analyzed by gas chromatography. The mole fraction of CO_2 in the gas phase (xCO_{2eq}) was determined after the catalytic conversion of CO_2 to CH_4 with a flame ionization detector through comparison with a calibration curve based on CO_2 in air standards. These standards were subsequently intercalibrated with standards maintained by Taro Takahashi and Dave Chipman at the Lamont-Doherty Earth Observatory (LDEO).

Erroneously, in the original work (Johnson et al. 1990), no provision was made to measure the total gas phase pressure in the serum bottle after equilibration (P_{eq}). Because P_{eq} was not measured during WOCE Section P6, it had to be estimated. This was done by first calculating the moles of N_2, O_2, and Ar in the liquid phase prior to equilibration using potential temperature, the measured O_2 concentrations, and by assuming that each water sample was saturated at the surface with N_2 and Ar with moist air at 1 atm at the potential temperature of the sample. Next, the total number of moles of each gas in the introduced gas phase was calculated. Hence the total number of moles of each gas present in the closed system (serum-bottle) was known. After equilibration, a small correction for glass expansion and the phase ratio volume change caused by the change in temperature during equilibration (usually warming) was applied. The partial pressure of each gas at the equilibration temperature (20°C) was then calculated from the total number of moles for each gas, and these gas partial pressures along with the equilibrium partial pressure of water vapor were summed to give P_{eq} in the headspace after equilibration. Then xCO_{2eq} and P_{eq} were multiplied to convert xCO_{2eq} to pCO_2 hereafter called pCO_{2eq}. Subsequent laboratory tests (C. Neill and D. Wallace, unpublished data) confirmed that the serum bottles were not subject to leakage and that the predicted pressure closely matched the actual headspace pressure. The close correspondence between measured and predicted headspace pressure has also been confirmed during extensive field tests (see Neill et al. 1997).

TCO_2 was measured on an unequilibrated duplicate sample, and the TCO_2 of the liquid phase after equilibration (repartitioning of CO_2 between the gas and liquid phases) was calculated using a mass balance approach (hereafter designated TCO_{2eq}). The carbonate alkalinity (CA) of the equilibrated sample was calculated using pCO_{2eq} and TCO_{2eq} with the thermodynamic constants of Roy et al. (1993) and software developed by Lewis and Wallace (1998). Because carbonate alkalinity is conserved during the equilibration, the derived CA (μmol/kg) is the in situ value prior to equilibration. Hence both the in situ TCO_2 (measured independently by coulometry) and CA are known for each sample prior to the equilibration, and these two parameters were used to calculate the sample in situ pCO_2 at the equilibration temperature using the Lewis and Wallace (1998) software and the Roy et al. (1993) constants. The pCO_2 in μatm is reported at the equilibration temperature and the equilibration temperature is also reported. Subsequently, the nutrient data became available and Total Alkalinity (TALK) was also calculated for each sample according to DOE procedures (1994) using the software given by Lewis and Wallace (1998). TALK values are not reported in this NDP.

The precision of the pCO_2 determination and the TALK calculated from pCO_2 and TCO_2 was assessed, when possible, according to the same procedures used for TCO_2. The precision of the pCO_2 determination and the derived TALK is given in Table 11 as follows:

- "between-sample" precision (σ_{bs}) for pCO_2, which is the mean absolute difference between duplicates ($n = 2$) of K samples drawn from the same Niskin bottle;
- the pooled standard deviation (S_p^2) for pCO_2, calculated according to Youden (1951) where K was the number of samples with duplicates analyzed ($n \geq 2$), n was the total number of replicates analyzed from K samples, and $n - K$ was the degrees of freedom (d.f.);
- the geometric mean (GM) of the relative standard deviation (Rel. S. D.) for pCO_2 from K samples with duplicates ($n \geq 2$) analyzed where the Rel. St. Dev. (%) was: (S. D. / mean) × 100;
- the pooled standard deviation (S_p^2) for TALK calculated according to Youden (1951) from K pCO_2 samples with duplicates analyzed ($n \geq 2$), with n being the total number of TALK calculated from K samples with $n - K$ degrees of freedom; and
- the Rel. S. D. (%) for TALK calculated as (S_p^2 / mean TALK) × 100.

Table 11. Summary of sample precision for pCO_2 and the derived TALK
for WOCE Section P6

Leg	σ_{bs} (K) (±µatm)	S_p^2 (±µatm)	K	n	d.f.	GM (K) (%)	TALK (S_p^2) (±µmol/kg)	Rel. S. D. (%)
P6E	13.4 (19)	12.8	21	48	27	0.70 (21)	2.36	0.10
P6C	23.5 (45)	19.8	55	127	72	0.97 (55)	3.82	0.16
P6W	16.0 (32)	15.2	32	66	34	0.88 (33)	3.08	0.13
All	19.0 (96)	17.4	109	243	134	0.88 (109)	3.39	0.14

In all, duplicates for 109 of the 808 pCO_2 samples were taken during WOCE Section P6. Based on these samples, the sample precision (S_p^2) for pCO_2 was ±17.4 µatm. Because of the large dynamic range of the pCO_2 measurements (>1000 µatm), the geometric mean of the Rel. S. D. was considered to be the best measure of overall sample precision on a percentage basis (±0.88%). For the derived variable TALK, the sample precision (S_p^2) was ±3.39 µmol/kg and the Rel. St. Dev. [(S_p^2/ mean) × 100] was 0.14%. The corresponding result for TCO_2 is approximately 0.08%.

The best precision was found for P6E and the worst for P6C, which is consistent with the difficulties for the pCO_2 system reported during the P6C cruise. However, the precision for the TALK derived from the pCO_2 and the greater imprecision of the TALK determination in comparison with the precision of the TCO_2 determination, particularly for P6W (factor of 2), were consistent with results from other WOCE cruises (Millero et al. 1998).

3.3.1 Crossover Analysis for pCO_2 Measurements Made During WOCE Section P6

Because the pCO_2 method was still under development and because of the instrument difficulties experienced during the WOCE Section P6, additional QC-QA assessment was required. Final results of the P6 pCO_2 analyses were checked by comparing the deep water results with those obtained on other WOCE cruises that intersected the P6 line. With this test it was assumed that deep and bottom water results have not changed at a given location over the

relatively short time interval of a few years separating the different cruises.

The stations selected for each crossover are those which are close to the crossover point and on which carbon measurements were made. The number of stations selected was somewhat subjective but was such that sufficient measurements were present for the analysis without getting too far away from the crossover location. In all cases the stations were within approximately 1° of latitude and longitude of the crossover point. Table 12 lists the stations used for each crossover.

Once the stations were chosen the results were plotted against potential density referenced to 3000 dbar (σ3). Only data from pressures greater than 2500 dbar were included in order to minimize the influence of possible lateral gradients. A smooth curve was fitted to the combined station data from each leg so long as there were seven or more data points that could be used for the fit. The fitting curve chosen was a "robust loess" function designed to minimize the influence of outliers (Feely et al. 1999). In cases having fewer than 7 points, linear segments were used to "connect the dots." Only data which had been marked with a quality control flag of 2 (good) or 6 (replicate) were included in the analyses. Reported pCO_2 results were converted to fCO_2 using the Weiss function (Weiss 1974) and the measured temperature prior to the comparison. fCO_2 values are not reported in this NDP.

In order to quantitatively estimate the mean difference between legs, each of the two fitted curves was evaluated at 50 evenly spaced intervals covering the range of space common to the selected stations from both legs. The 50 differences were then averaged. Table 12 summarizes the mean differences and standard deviations for each crossover, and indicates the differences in terms of the cruise leg designations.

Table 12. WOCE Section P6 fCO_2 crossover results

Crossover no.[a]	Cruise 1	Stations	Cruise 2	Stations	Differences
66a	P16S/P17S	179	P6W	108	6.7 ± 8.6
66c	P16A/P17A	119	P6W	108	7.6 ± 11.3
76	P18	73	P6E	56, 58	-12.9 ± 6.4
81	P19C	299	P6E	32, 34, 36	3.6 ± 7.3

[a]Crossover number taken from the Global Ocean Data Analysis Project (GLODAP) list for the entire Pacific Ocean (Lamb et al. 2001).

Samples from one of the intersecting cruises, P18, were analyzed by Rik Wanninkhof of the Atlantic Oceanographic and Meteorological Laboratory while the other three were analyzed by scientists from Taro Takahashi's group of LDEO. Previous crossover tests have indicated that the P18 fCO_2 results may be somewhat low as a result of minor sample loss, and the checks preformed at CDIAC tend to support that finding. Differences between the P6 results and those measured by the LDEO group are well within the precision (Table 12) of the technique.

Based on these checks, the prototype pCO_2 method appears to have performed adequately, and no additional corrections to the pCO_2 data have been made. Nevertheless, the P6 Section work showed that the pCO_2 method could be improved. Before the next deployment in 1994, the pCO_2 method incorporated automated and highly accurate measurements of P, P_{eq}, and analytical temperatures throughout, rigorous control of the phase volume ratio and the headspace gas composition prior to equilibration, and new software (Neill et al. 1997). Figure 7 summarizes the analytical results as a contour section plot of the pCO_2 data from the WOCE Section P6.

3.4 Radiocarbon Measurements

During the R/V *Knorr* expedition along WOCE Section P6, 649 accelerator mass spectrometry (AMS) delta ^{14}C samples were collected at 30 stations. In addition 17 replicate measurements of ^{14}C were performed. Sampling of ^{14}C during the cruise was carried out by the scientists from the Ocean Tracer Laboratory at Princeton University, with R. Key as the principal investigator for these data. For a detailed description of the methods and instrumentation used for ^{14}C measurements please read the reprint of pertinent literature: "P6 Final Report for AMS [14]C Samples" in Appendix A of this documentation.

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 *Knorr* cruise along WOCE Section P6 in the South Pacific Ocean.

1.   The final carbon-related data were provided to CDIAC by D. W. R. Wallace and K. M. Johnson of Brookhaven National Laboratory. 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. 8–13). 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. 14), carefully examined, and compared with plots from previous expeditions in the Pacific 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 < 1 or > 12; DAY < 1 or > 31; YEAR < or > 1992; TIME < 0000 or > 2400; LATITUDE < −25.000 or > −32.000; LONGITUDE < 150.000 or > −80.000.

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.

5. HOW TO OBTAIN THE DATA AND DOCUMENTATION

This database (NDP-077) 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 160.91.18.18
Login: "anonymous" or "ftp"
Password: your e-mail address
ftp> cd pub/ndp077/
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.

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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 nine files that comprise this NDP (see Table 13). Because CDIAC distributes the data set in several ways (via the Web, CDIAC's online ordering system, or anonymous FTP), each of the nine files is referenced by both an ASCII file name, which is given in lowercase, bold-faced type (e.g., **ndp077.txt**), and a file number. The remainder of this section describes (or lists, where appropriate) the contents of each file.

Table 13. Content, size, and format of data files

File number, name, and description	Logical records	File size in bytes
1. **ndp077.txt**: a detailed description of the cruise network, the two FORTRAN 90 data-retrieval routines, and the six oceanographic data files	1,881	118,354
2. **stainv.for**: a FORTRAN 90 data-retrieval routine to read and print **p6esta.dat** (File 4), **p6csta.dat** (File 5), and **p6wsta.dat** (File 6)	45	1,337
3. **p6ecwdat.for**: a FORTRAN 90 data-retrieval routine to read and print **p6e.dat** (File 7), **p6c.dat** (File 8), and **p6w.dat** (File 9)	54	2,242
4–6. **p6esta.dat, p6csta.dat, p6wsta.dat**: a listing of the station locations, sampling dates, and sounding bottom depths for each station of the WOCE Sections P6E, P6C, and P6W	82 124 90	6,146 9,338 6,754
7–9. **p6e.dat, p6c.dat, p6w.dat**: hydrographic, carbon dioxide, and chemical data from all stations occupied on WOCE Sections P6E, P6C, and P6W	2,353 3,982 1,564	412,952 699,656 274,088
Total	10,175	1,530,867

7.1 ndp077.txt (File 1)

This file contains a detailed description of the data set, the two FORTRAN 90 data-retrieval routines, and the six 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 **p6*sta.dat** (Files 4–6). 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 **p6*sta.dat** in Sect. 7.4.

```
c******************************************************************
c* FORTRAN 90 data retrieval routine to read and print the files
c* named "p6*sta.dat" (File 4-6).
c******************************************************************

c*Defines variables*

      INTEGER  stat, cast, depth
      REAL latdcm, londcm
      CHARACTER expo*9, sect*4, date*10, time*4
      OPEN (unit=1, file='p6*sta.dat')
      OPEN (unit=2, file='p6*.sta')
      write (2, 5)

c*Writes out column labels*

5     format (1X,'EXPOCODE',3X,'SECT',1X,'STNBR',2X,'CAST',9X,
    3 'DATE',2X,'TIME',2X,'LATITUDE',2X,'LONGITUDE',2X,
    4 '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 (A9, 3X, A4, 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, 3X, A4, 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 p6ecwdat.for (File 3)

This file contains a FORTRAN 90 data-retrieval routine to read and print **p6*.dat** (Files 7–9). 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
p6*.dat in Sect. 7.5.

```
c*********************************************************************
c* FORTRAN 90 data retrieval routine to read and print the files
c* named "p6*.dat" (Files 7-9).
c*********************************************************************

c*Defines variables*

      CHARACTER qualt*12, bot*7
      INTEGER sta, cast, samp
      REAL pre, ctdtmp, ctdsal, ctdoxy, theta, sal, oxy, silca
      REAL nitrat, nitrit, phspht, dc14, c14er, tco2, pco2, pco2tmp
      OPEN (unit=1, file='p6e.dat')
      OPEN (unit=2, file='p6e.data')
      write (2, 5)

c*Writes out column labels*

5     format (2X,'STNNBR',2X,'CASTNO',2X,'SAMPNO',2X,'BTLNBR',
     1 2X,'CTDPRS',2X,'CTDTMP',2X,'CTDSAL',2X,'CTDOXY',3X,'THETA',
     2 4X,'SALNTY',2X,'OXYGEN',2X,'SILCAT',2X,'NITRAT',2X,'NITRIT',
     3 2X,'PHSPHT',2X,'DELC14',2X,'C14ERR',2X,'TCARBN',4X,'PCO2',1X,
     4 'PCO2TMP',7X,'QUALT1',/,36X,'DBAR',2X,'ITS-90',2X,'PSS-78',
     5 1X,'UMOL/KG',2X,'ITS_90',4X,'PSS-78',1X,5('UMOL/KG',1X),
     6 1X,'/MILLE',2X,'/MILLE',1X,'UMOL/KG',4X,'UATM',3X,'DEG_C',12X,
     7 '*',/,25X,'*******',17X,2('*******',1X),10X,7('*******',1X),
     8 8X,2('*******',1X),19X,'*')

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, dc14, c14er, tco2, pco2, pco2tmp, qualt

10    format (5X, I3, 7X, I1, 6X, I2, 1X, A7, 1X, F7.1, 1X, F7.4,
     1 1X, F7.4, 1X, F7.1, 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, F7.1,
     3 1X, F7.1, 1X, F7.1, 1X, A12)

      write (2, 20) sta, cast, samp, bot, pre, ctdtmp,
     1 ctdsal, ctdoxy, theta, sal, oxy, silca, nitrat, nitrit,
     2 phspht, dc14, c14er, tco2, pco2, pco2tmp, qualt

20    format (5X, I3, 7X, I1, 6X, I2, 1X, A7, 1X, F7.1, 1X, F7.4,
     1 1X, F7.4, 1X, F7.1, 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, F7.1,
     3 1X, F7.1, 1X, F7.1, 1X, A12)

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

```
        stop=2)
        stop
        end
```

7.4 p6*sta.dat (Files 4–6)

These files, **p6esta.dat**, **p6csta.dat**, and **p6wsta.dat,** provide station inventory information for each station occupied during the R/V *Knorr* cruise along WOCE Sections P6E, P6C, and P6W. Each line in the files contains an expocode, section number, station number, cast number, sampling date (month/date/year), sampling time, latitude, longitude, and sounding depth. The files are 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*4, 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, 3X, A4, 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	4	13	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 p6*.dat (Files 7–9)

These files, **p6e.dat**, **p6c.dat**, and **p6w.dat**, provide hydrographic, carbon dioxide, and chemical data for all stations occupied during the R/V *Knorr* cruise along WOCE Sections P6E, P6C, and P6W. 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, bottle oxygen, silicate, nitrate, nitrite, phosphate, $\Delta^{14}C$, ^{14}C error, TCO_2, pCO_2, pCO_2 temperature, and data-quality flags. The files are sorted by station number and pressure and can be read by using the following FORTRAN 90 code (contained in **p6ecwdat.for,** File 3):

```
      CHARACTER qualt*12, bot*7
      INTEGER sta, cast, samp
      REAL pre, ctdtmp, ctdsal, ctdoxy, theta, sal, oxy, silca
      REAL nitrat, nitrit, phspht, dc14, c14er, tco2, pco2, pco2tmp

      read (1, 10, end=999) sta, cast, samp, bot, pre, ctdtmp,
    1 ctdsal, ctdoxy, theta, sal, oxy, silca, nitrat, nitrit,
    2 phspht, dc14, c14er, tco2, pco2, pco2tmp, qualt


10    format (5X, I3, 7X, I1, 6X, I2, 1X, A7, 1X, F7.1, 1X, F7.4,
    1 1X, F7.4, 1X, F7.1, 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, F7.1,
    3 1X, F7.1, 1X, F7.1, 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	22	24
bot	Character	7	26	32
pre	Numeric	7	34	40
ctdtmp	Numeric	7	42	48
ctdsal	Numeric	7	50	56

ctdoxy	Numeric	7		58	64
theta	Numeric	7		66	72
sal	Numeric	9		74	82
oxy	Numeric	7		84	90
silca	Numeric	7		92	98
nitrat	Numeric	7		100	106
nitrit	Numeric	7		108	114
phspht	Numeric	7		116	122
dc14	Numeric	7		124	130
c14er	Numeric	7		132	138
tcarb	Numeric	7		140	146
pco2	Numeric	7		148	154
pco2tmp	Numeric	7		156	162
qualt	Character	12		164	175

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);

dc14[a] is the radiocarbon delta ^{14}C (per mille);

c14er is the error of delta ^{14}C (percent);

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

pco2[a]   is the partial pressure of CO_2 (μatm);

pco2tmp   is the temperature of equilibration of the pCO_2 samples in equilibrator (°C);

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.

APPENDIX A:

REPRINT OF PERTINENT LITERATURE