

**GLOBAL OCEAN DATA ANALYSIS PROJECT (GLODAP): RESULTS AND DATA**

Contributed by

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## ACRONYMS

AOML	Atlantic Oceanographic and Meteorological Laboratory, NOAA
AOU	apparent oxygen utilization
AMS	accelerator mass spectrometry
ASW	artificial seawater
BNL	Brookhaven National Laboratory
$^{14}\text{C}$	radiocarbon
CDIAC	Carbon Dioxide Information Analysis Center
CFC	chlorofluorocarbon
$\text{CO}_2$	carbon dioxide
CTD	conductivity, temperature, and depth sensor
CRM	certified reference material
DIC	dissolved inorganic carbon
DOE	U.S. Department of Energy
DQE	data quality evaluation
$f\text{CO}_2$	fugacity of $\text{CO}_2$
GC	gas chromatograph
GEOSECS	Geochemical Ocean Sections Study
GLODAP	Global Ocean Data Analysis Project
JGOFS	Joint Global Ocean Flux Study
LAS	Live Access Server
LDEO	Lamont-Doherty Earth Observatory
MLR	multi-parameter linear regression
NDIR	non-dispersive infrared analyzer
NDP	numeric data package
NOAA	National Oceanic and Atmospheric Administration
NOSAMS	National Ocean Sciences AMS Facility
NSF	National Science Foundation
OACES	Ocean-Atmosphere Carbon Exchange Study
OCMIP	Ocean Carbon-Cycle Model Intercomparison Project
ODV	Ocean Data View (software)
OMP	optimum multiparameter
ORNL	Oak Ridge National Laboratory
PALK	potential alkalinity
$\text{pCO}_2$	partial pressure of $\text{CO}_2$
PI	personal investigator
PMEL	Pacific Marine Environmental Laboratory
PNL	Pacific National Laboratory
PU	Princeton University
QA	quality assurance
QC	quality control
R/V	research vessel
RSMAS	Rosenstiel School of Marine and Atmospheric Sciences
SAVE	South Atlantic Ventilation Experiment
SIO	Scripps Institution of Oceanography

SOMMA	single-operator multi-parameter metabolic analyzer
SW	seawater
TALK	total alkalinity
TCO <sub>2</sub>	total inorganic carbon dioxide
TTO	Transient Tracers in the Oceans
UM	University of Miami
UNESCO	United Nations Educational, Scientific, and Cultural Organization
UPMC	Université Pierre et Marie Curie, Paris, France
WHOI	Woods Hole Oceanographic Institution
WOCE	World Ocean Circulation Experiment
WHP	WOCE Hydrographic Program

## ABSTRACT

Sabine, C. L., R. M. Key, A. Kozyr, R. A. Feely, R. Wanninkhof, F. J. Millero, T.-H. Peng, J. L. Bullister, and K. Lee. 2005. Global Ocean Data Analysis Project: Results and Data. ORNL/CDIAC-145, NDP-083. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, 110 pp. doi: 10.3334/CDIAC/otg.ndp083

During the 1990s, ocean sampling expeditions were carried out as part of the World Ocean Circulation Experiment, the Joint Global Ocean Flux Study, and the Ocean Atmosphere Carbon Exchange Study. Most of the cruises included various inorganic carbon species among the suite of routinely measured parameters. Both during and after the field work, a group of U.S. scientists collaborated to synthesize the data into easily usable and readily available products. This collaboration is known as the Global Ocean Data Analysis Project (GLODAP).

Both measured results and calculated quantities were merged into common-format data sets, segregated by ocean. The carbon data were subjected to rigorous secondary quality control procedures, beyond those typically performed on individual cruise data, to eliminate systematic biases in the basin-scale compilations. For comparison purposes, each ocean data set included results from a small number of high-quality historical cruises. The calibrated 1990s data were used to estimate anthropogenic CO<sub>2</sub>, potential alkalinity, chlorofluorocarbon (CFC) water mass ages, CFC partial pressure, bomb-produced radiocarbon, and natural radiocarbon. The calibrated-merged data were used to produce objectively gridded global property maps designed to match existing climatologies for temperature, salinity, oxygen, and nutrients. Both the data sets and the gridded products are available from the Carbon Dioxide Information Analysis Center (CDIAC). Here we summarize important details of the data assembly, calibration, calculations, and mapping.

The synthesis was carried out one ocean at a time, progressing from the Indian to the Pacific and ending with the Atlantic. The entire synthesis required about five years. During that period, new methods were developed and old ones modified. At the same time, the data set itself changed and expanded. Many of the GLODAP results are already published. Rather than repeat what is published, we concentrate here on summarizing important details of the data assembly and mapping. In particular, we focus on the procedural differences that evolved as the individual basin data sets were compiled and developments in the data set that have not been covered in the individual publications. Some of the GLODAP publications are attached as appendices.

The GLODAP data set described here (Gv1.1) is available free of charge as a numeric data package (NDP-83) from CDIAC. The data, and any subsequent updates, are also available through the GLODAP web site ([http://cdiac.ornl.gov/oceans/glodap/Glodap\\_home.htm](http://cdiac.ornl.gov/oceans/glodap/Glodap_home.htm)). The GLODAP bottle data files are available in flat ASCII file data format, in Ocean Data View (ODV) format, and through the CDIAC live access server (LAS); the gridded data files are available in flat ASCII and NetCDF data file formats and through CDIAC LAS.

**Keywords:** Global CO<sub>2</sub> survey; carbon cycle; carbon dioxide; radiocarbon; anthropogenic CO<sub>2</sub>; data synthesis; data interpretations; crossover analysis; crossover stations; data adjustments; gridded carbon fields.



# 1. INTRODUCTION

During the 1990s, three major ocean sampling expeditions were completed: the World Ocean Circulation Experiment (WOCE), the Joint Global Ocean Flux Study (JGOFS), and the Ocean-Atmosphere Carbon Exchange Study (OACES). WOCE and JGOFS were international collaborations, while OACES was a U.S. National Oceanographic and Atmospheric Administration (NOAA) project. OACES and WOCE were survey-type studies, while JGOFS was generally process-oriented. Among the goals of these programs were specific objectives to better understand ocean circulation, biogeochemistry, and air-sea exchange processes for carbon; to provide a baseline for determining future changes in the ocean; and to develop numerical models that could be used to predict the influence of anthropogenic factors on global climate change. The three programs were planned, organized, and funded differently; however, there was significant coordination and collaboration among them. For instance, the carbon sampling and analysis (total CO<sub>2</sub>, TALK, pH and/or pCO<sub>2</sub>) on U.S. WOCE cruises, which were primarily funded by the National Science Foundation (NSF), were part of a JGOFS project that was primarily funded by the U.S. Department of Energy (DOE). With a few exceptions, the three programs covered different ocean regions, thus improving the combined global coverage.

Each program incorporated elements designed to provide information on global climate change questions. During the field work phase of these three programs, a U.S. CO<sub>2</sub> Science Team (Table 1, in Section 10 “Tables”), composed of investigators making carbon measurements, coordinated and directed the carbon measurement components of the survey cruises. Similar, less formally organized groups of U.S. investigators coordinated sampling, analysis, and calibration for the other tracers. Once the field work was completed, some of the CO<sub>2</sub> Science Team plus others cooperated to produce a merged-calibrated data set that included all the tracers discussed below and to estimate various parameters pertinent to global climate change. At various stages, other investigators provided significant input to specific portions of the compilation. This collaboration continues and is known as the Global Ocean Data Analysis Project (GLODAP). Both the members of the GLODAP team and additional contributors are listed in Table 2. The GLODAP goals were (and remain) as follows:

1. To produce an easily usable, fully calibrated data set specifically designed to study global-scale carbon-related issues;
2. To make uniformly calculated estimates of the oceanic distribution, changes, and inventory of anthropogenic CO<sub>2</sub>;
3. To better describe the aqueous biogeochemistry of inorganic carbon in the ocean;
4. To describe the oceanic distribution and inventory of natural and bomb-produced radiocarbon and to investigate changes in the bomb transient;
5. To describe the oceanic distribution and inventory of various chlorofluorocarbons (CFCs) and to investigate the application of CFCs to ocean ventilation;
6. To produce gridded fields of the various measured and calculated parameters that could be used as boundary conditions for numerical ocean models, or against which model performance could be judged;
7. To make both the data and the gridded fields publicly available.

Subsets of the data described here have been used to address the second and third goals. That work was done on an ocean-by-ocean basis as the data and estimated quantities became available. Sabine et al. (1999, 2002a) and Lee et al. (2003) estimated the anthropogenic CO<sub>2</sub> distribution and inventory for the Indian, Pacific, and Atlantic Oceans, respectively. The global synthesis for anthropogenic CO<sub>2</sub> was given by Sabine et al. (2004). The inorganic carbon chemistry for the three oceans was described by Sabine et al. (2002b), Feely et al. (2001, 2002) and Chung et al. (2003, 2004). Feely et al. (2004) published a global summary of the carbonate work. Millero et al. (2002) evaluated the thermodynamic inorganic carbon dissociation constants, using a subset of the GLODAP data where the carbon system was overdetermined (i.e. more than two carbon parameters were measured). Finally, Key et al. (2004) summarized the data assembly and mapping procedures, discussed large-scale property distributions and estimated global

inventories. Significant portions of this document are excerpted from previously published manuscripts.

Because of the required analytical time, the radiocarbon interpretation has lagged the inorganic carbon analysis significantly. However, the Pacific radiocarbon data have been published (Key 1996; Key et al. 1996, 2002; Stuiver et al., 1996) in addition to brief scientific summaries (Key 1997, 2001; Schlosser et al. 2001, Matsumoto and Key 2004; Matsumoto et al. 2004). Additionally, Rubin and Key (2002) published an improved method of separating the natural and bomb-produced radiocarbon that was based on the strong linear correlation between potential alkalinity and natural radiocarbon.

Though not associated with GLODAP, Willey et al. (2004) produced the first global CFC inventory estimate using a subset of the GLODAP data base; and those results are completely compatible, within estimated error, of those produced during GLODAP. Preliminary versions of the gridded GLODAP fields were used in the Ocean Carbon-Cycle Model Intercomparison Project (OCMIP). Orr et al. (2001) examined anthropogenic CO<sub>2</sub> uptake during the first-phase OCMIP that included four different models. Dutay et al. (2002) compared the performance of 13 ocean models in a study of upper ocean ventilation using CFC-11. Additional information about OCMIP is available (<http://www.ipsl.jussieu.fr/OCMIP/>).

To date, 33 peer-reviewed publications and many more technical documents have resulted either in part or totally from work done as part of GLODAP. Here we try to summarize information relating to construction of the database, giving emphasis to important but unpublished details and enumerating some of the subtle procedural developments that occurred as the program progressed. First, we describe the data assembly and calibration procedures, and then the objective mapping method. Although the GLODAP data set will continue to evolve and improve, we felt it was important to fully document the first public release of these data, Gv1.1, and the processes that ultimately led to this product. Both the data and the gridded products, as well as significant other unpublished information, are freely available via the internet ([http://cdiac.esd.ornl.gov/oceans/glodap/Glodap\\_home.htm](http://cdiac.esd.ornl.gov/oceans/glodap/Glodap_home.htm)), where future versions of the GLODAP data set will be posted.

Users of the GLODAP bottle data sets are strongly cautioned that these data are not a simple merge of individual cruise files but are a synthetic product. In many cases, adjustments/calibrations have been applied to the data. The adjustments were based on three important assumptions: (1) that the deep ocean hydrography and circulation have been in steady state for the time period covered by the data; (2) that oceanic property distributions, away from the surface and other boundaries, tend to be smooth; and (3) that the experience of the authors (and others) was of value in determining the relative quality of various measurements. The first assumption was not applied to parameters in regions known to be changing as a result of anthropogenic influences such as total CO<sub>2</sub> (TCO<sub>2</sub>) and the transient tracers. The second and third assumptions were important for both the initial quality control (QC) check and the various adjustments. Both were applied somewhat subjectively and non-uniformly because numerous people were involved.



## 2. DATABASE CONSTRUCTION

### 2.1 Data Collection

Cruise data included in Gv1.1 were chosen to provide high-quality global coverage. With a few exceptions, the quality of the WOCE-era hydrographic data meet WOCE standards as described in Joyce and Corry (1994). Most of the data sets were received from the data centers associated with the individual research programs (WOCE, OACES, JGOFS). Additional data were received directly from chief scientists and individual investigators. Significant priority was given to cruises that included the carbon parameters; however, a limited number of cruises without carbon were included to provide more complete hydrographic, nutrient and oxygen coverage. cursory investigation indicates that the Gv1.1 hydrography, nutrients, and oxygen are sufficiently dense to reasonably approximate larger (annual mean) compilations such as those provided by Conkright et al. (2002). *Note, however, Gv1.1 has a seasonal bias in shallow water that should be considered in interpreting data from this depth zone.* Metadata for the cruises, investigators, and measurements are summarized by ocean in Tables 3–5. Information on assembly of the data base can be found in Key et al. (2004; reprinted as Appendix A).

Summary statistics for some of the data included in Gv1.1 are given in Table 6. We use “WOCE stations/cruises/data” generically, to refer to stations occupied as part of either WOCE, JGOFS or OACES field work and slightly older cruises officially designated as WOCE sections (except in cases where differentiation is important). “Historical stations/cruises” refers to all other data. No data older than GEOSECS (1972–1978) are included in the compilation. Gv1.1 station locations are shown in Fig. 1 with color indicating WOCE era (black) vs. historic (red) stations.

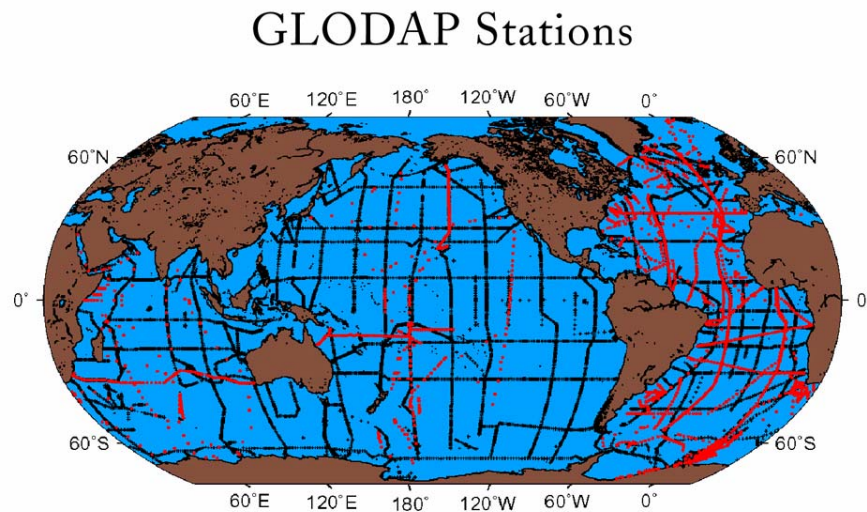


Fig. 1. GLODAP data base station locations map.

### 2.2 Included parameters

Parameters and units included in the GLODAP bottle data files are listed in Table 7. Here we give a brief summary of the analytical measurement and calibration procedures.

#### 2.2.1 Basic Hydrographic Parameters

All of the cruises in Gv1.1 included measurements of pressure, temperature, salinity, oxygen, and the nutrients. For the vast majority of the samples pressure and temperature data are from CTD measurements while salinity and nutrients samples were from individual Niskin-type bottles collected with a Rosette. Significant effort was devoted to assuring that data units were consistent. This was particularly difficult

for the nutrients. In many cases we directly contacted the technician who made the measurements for verification. All discrepancies were reported to the various data collection offices. Details on CTD calibration and measurement precision for nutrients, oxygen, and salinity for most of the WOCE era cruises can be found in the final reports available at the program offices (see reference footnotes in the cruise summary tables).

Some of the historic cruises (GEOSECS, TTO, SAVE, INDIGO) and several of the WOCE cruises (mostly Pacific) include results from the large-volume Gerard barrels used to collect radiocarbon samples. Unfortunately, there is no simple way in the merged data sets to discriminate between Rosette and Gerard samples. For the historic cruises, hydrographic data from Gerard barrels remain in the data set as originally reported. For the Pacific U.S. WOCE cruises, Gerard samples can be identified by bottle numbers greater than 80 (also true for the historic U.S. cruises). For these bottles, the measured salinity data were as good as the Rosette data and were retained. Gerard barrel nutrient measurements (usually just silicate) were made primarily as an indicator that the barrel closed at the desired depth. These measured (U.S. WOCE Gerard barrel) nutrient values were discarded and both nutrient and oxygen estimates for the Gerard samples were estimated by interpolation using Rosette samples from the same station. Details of the interpolation method were given in Key et al. (2004, Appendix A). German cruises (historic and WOCE era) did not use unique bottle numbers for large-volume samples. Additionally, tests they have run indicate that nutrient and oxygen results from their Gerard barrels are comparable to Niskin bottle data. Therefore, large-volume nutrient measurements from those cruises were retained.

### **2.2.2 Total Carbon Dioxide (TCO<sub>2</sub>)**

All TCO<sub>2</sub> samples that were retained in this synthesis work were analyzed by coulometric titration. The primary differences between the various groups were the sample volume used, the level of automation, and the primary calibration method. On many cruises the coulometer (UIC, Inc.) was coupled to a semi-automated sample analyzer (Johnson and Wallace 1992; Johnson et al. 1985, 1987, 1993, 1998a). The most common system, a single-operator multiparameter metabolic analyzer (SOMMA), was typically outfitted with a 20–30-mL pipette and was calibrated by filling a gas loop with a known volume of pure CO<sub>2</sub> gas, then introducing the gas into the carrier gas stream and performing subsequent coulometric titration (Johnson and Wallace 1992; Johnson et al. 1987, 1993, 1998a). Some systems were calibrated by analyzing sodium carbonate standards. TCO<sub>2</sub> systems that were not coupled with a semi-automated sample analyzer introduced the sample manually with a pipette or a syringe.

### **2.2.3 Total Alkalinity (TALK)**

All shipboard TALK measurements were made by potentiometric titration using a titrator and a potentiometer. TALK was determined either by characterizing a full titration curve (Brewer et al. 1986; Millero et al. 1993; DOE 1994; Ono et al. 1998) or by a single-point titration (Perez and Fraga 1987). Analytical differences were in the volume of sample analyzed, the use of either an open or closed titration cell, and the calibration methods. Results were obtained from different curve-fitting techniques such as Gran plots, nonlinear fitting, or single-point analysis.

In developing the GLODAP dataset, a decision was made to provide global datasets with two carbon parameters. Since TCO<sub>2</sub> was always one of the measured parameters on the carbon cruises, it was selected as the first parameter. A choice was made to have TALK be the second parameter, based on several factors. First, TALK was by far the most common second parameter measured. For example, every cruise in the Indian Ocean had TALK measurements. Second, although the precision of the *f*CO<sub>2</sub> and pH measurements was superior to that of the TALK measurements, there have been some lingering questions about the accuracy of these measurements (see Sections 6.3 and 6.4). Finally, TALK is a state variable (not affected by temperature and pressure changes) so it is a more useful parameter for generating gridded fields. This is important because the GLODAP gridded values do not include the temperature fields, and a mismatch between the GLODAP values used and the temperature fields used may lead to large errors in calculating other carbon parameters. Furthermore, since TALK is a state variable and not generally thought to be affected by the uptake of anthropogenic CO<sub>2</sub>, it is a common parameter used in modeling

(the GLODAP fields can be used for initializing models). Thus on cruises where TALK was not measured, it was calculated from  $\text{TCO}_2$  and whatever second parameter was measured and reported in the GLODAP database. Please refer to the ocean basin summary tables (Tables 3–5) to determine which cruises have calculated TALK values.

#### 2.2.4 Fugacity of $\text{CO}_2$ ( $f\text{CO}_2$ )

Two different types of instruments were used to measure discrete  $f\text{CO}_2$  samples. The main difference between the systems was the sample size. One system used ~500-mL samples equilibrated by bubbling the recirculated 50-mL headspace gas through the sample. The small-volume technique equilibrated a 10-mL headspace with a 120-mL sample. With each, an aliquot of seawater was equilibrated at a constant temperature of either 4 or 20°C with a head space of known initial  $\text{CO}_2$  content. Subsequently, the head space  $\text{CO}_2$  concentration was determined by a nondispersive infrared analyzer (NDIR) or by quantitatively converting the  $\text{CO}_2$  to  $\text{CH}_4$  and then analyzing the concentration using a gas chromatograph (GC) with a flame ionization detector. The initial  $f\text{CO}_2$  in the water was determined after correcting for loss (or gain) of  $\text{CO}_2$  during the equilibration process. This correction can be significant for large initial  $f\text{CO}_2$  differences between the head space and the water, and for systems with a large head-space-to-water volume ratio (Chen et al. 1995).

Because discrete  $f\text{CO}_2$  was measured only on a small subset of all the cruises and TALK was selected as the second parameter for the database,  $f\text{CO}_2$  values were used to calculate TALK on those cruises where it was not directly measured. The measured discrete  $f\text{CO}_2$  values are not presented in Gv1.1 but can still be found in the original datasets at CDIAC.

#### 2.2.5 pH

The pH measurements were determined by using pH electrodes or, more commonly, by a spectrophotometric method (Clayton and Byrne 1993) with m-cresol purple as the indicator and either scanning or diode array spectrophotometers.

Because discrete pH was measured only on a small subset of all the cruises, and TALK was selected as the second parameter for the database, pH values were used to calculate TALK on those cruises where it was not directly measured or could not be calculated from  $f\text{CO}_2$ . The measured pH values are not presented in Gv1.1, but can still be found in the original datasets at CDIAC.

#### 2.2.6 Chlorofluorocarbons

CFCs in air and seawater samples were measured onboard the ship using electron capture gas chromatography, based on techniques described in Bullister and Weiss (1988). Seawater for the CFC analysis was transferred from the water sample bottles into 100-cc glass syringes for storage and was typically analyzed within 24 hours of collection. For analysis, about 35cc of seawater from the syringe was transferred into the CFC extraction system. The CFCs in the water sample were extracted using a stream of purified nitrogen and collected in a cryogenic trap. The trap was subsequently heated and its contents injected into chromatographic columns for separation. CFC peaks were detected as they passed through the electron capture detector.

Gas-phase standards of known CFC content, stored in high-pressure cylinders, were analyzed frequently to calibrate the CFC analytical systems. Air samples were typically analyzed along the cruise track to evaluate the saturation levels of surface seawater and to compare with expected atmospheric CFC background levels at the time of the cruise. CFC concentrations in air samples are reported as mole fraction [in parts-per-trillion (ppt)]. Dissolved CFC concentrations in seawater are expressed as pmol/kg, (where 1 pmol = 1 picomole =  $10^{-12}$  mole).

Blank corrections applied to the dissolved CFC measurements were based on the analytical blank of the extraction systems, or on measurements made during the cruises in regions of the water column thought to be essentially CFC-free at the time of sampling. Details on the CFC blanks applied to the individual cruise data sets, as well as problems encountered during the cruises, were provided by the CFC principal investigators (PIs) at <http://whpo.ucsd.edu>

### 2.2.7 Carbon-14

Both large-volume (~250-L) and small-volume (~500-mL) sample radiocarbon measurements are included in Gv1.1. Almost all of the historic results were large-volume samples. For the WOCE-era samples, all of the Indian Ocean results are small volume; almost all of the Atlantic Ocean results are small volume; and in the Pacific, large-volume samples were used for most of the deep water results and small-volume for the thermocline results. Large-volume samples were analyzed using traditional  $\beta$ -counting techniques. All of the U.S. large-volume radiocarbon analyses (both historic and WOCE) were made at the University of Miami or the University of Washington (G. Östlund and M. Stuiver, respectively). Small-volume samples were analyzed by accelerator mass spectrometry (AMS). All of the U.S. AMS measurements were made at the National Ocean Sciences AMS (NOSAMS) facility at Woods Hole Oceanographic Institution.

Tests have not been extensive; however, existing results indicate that there is no systematic difference between the large-volume and small-volume analyses. Additionally, the measurement uncertainty for the two sample types is approximately the same. Measurement uncertainty is included in Gv1.1 for each sample; however, the total uncertainty for all of the radiocarbon data is approximately 4‰.

Significant detail about the radiocarbon data can be found in the final cruise reports. In the Pacific, individual reports were prepared for each U.S. WOCE cruise, and these are available at the WOCE web site (<http://whpo.ucsd.edu/>). Since the Indian Ocean survey was carried out as a single continuous expedition, only one report was prepared. The final report for the Indian Ocean radiocarbon results (Key and Quay 2002) is available from the GLODAP publications web site (<http://cdiac.esd.ornl.gov/oceans/glodap/pubs.htm>). WOCE-era radiocarbon sampling in the Atlantic was very limited relative to the other basins because of insufficient funding and manpower and because the TTO and SAVE programs during the 1980s provided reasonable coverage. Gv1.1 Atlantic radiocarbon gridded maps are therefore based on results from these two previous programs.

### 2.2.8 Carbon-13

Carbon-13 was not a core tracer for WOCE, JGOFS, or OACES; however, P. Quay (University of Washington) was funded to make measurements on several legs. The majority of the  $\delta^{13}\text{C}$  measurements carried out during the survey were complimentary to  $\Delta^{14}\text{C}$  measurements. That is, the measurements were made so that  $\Delta^{14}\text{C}$  could be precisely calculated. During development of the AMS  $\Delta^{14}\text{C}$  procedure at NOSAMS, A. McNichol modified the  $\delta^{13}\text{C}$  measurement procedure in such a way that the  $\delta^{13}\text{C}$  data were almost as high in quality as samples collected specifically for  $\delta^{13}\text{C}$  analysis. The end result of this improvement was a global  $\delta^{13}\text{C}$  data set with almost the same distribution as the  $\Delta^{14}\text{C}$  data.

GLODAP v1.1 contains most of the  $\delta^{13}\text{C}$  measurements made during the survey; however, these data have not been thoroughly QCed. Additionally, and more important, GLODAP Gv1.1 contains the  $\delta^{13}\text{C}$  measurements that were made on the large-volume samples used for deep  $\Delta^{14}\text{C}$  measurements in the deep Pacific. The large-volume  $\delta^{13}\text{C}$  data are precise but are not sufficiently accurate to be of any value for oceanographic interpretation. The  $\delta^{13}\text{C}$  data will be fully screened for the next version of the GLODAP data; however, in the interim, a reasonable data set can be obtained by simply discarding all  $\delta^{13}\text{C}$  values from large-volume samples—that is, samples with bottle number greater than 80. One exception to this rule is that the large-volume sample bottle numbers from Meteor cruises cannot be identified this way. Fortunately, the  $\delta^{13}\text{C}$  results from these samples are significantly better than the norm because a different analytical procedure was used.

### 2.3 Routine Calculations

Whenever a new set of cruise data was obtained, all routinely calculated parameter values (potential temperature, potential density anomaly, and apparent oxygen utilization) were discarded and recalculated. This guaranteed as much uniformity as possible for these values. Potential temperature calculations used the functions of Fofonoff (1977) and the adiabatic lapse rate from Bryden (1973). Potential density calculations used the United Nations Educational, Scientific, and Cultural Organization function

(UNESCO 1981). For apparent oxygen utilization (AOU), we used the solubility function of Garcia and Gordon (1992). In a very few cases, data sets did not include in situ temperature but only potential temperature. In those instances, the potential temperature was retained.

To calculate TALK values from  $\text{TCO}_2$  and one other carbon parameter, the constants of Mehrbach et al. (1973) as a refit by Dickson and Millero (1987) were used, along with equilibrium constants for other components (e.g., boric acid dissociation, solubility of  $\text{CO}_2$ , water hydrolysis, and phosphoric and silicic acid dissociation) recommended in Millero (1995).



### 3. DATA EVALUATION

As the ocean data sets were assembled, consistency was checked using a variety of approaches. Because the quality of the input data directly determines the quality of the final products, a great deal of effort was expended in evaluating the individual cruise data to ensure that all of the cruises were as consistent and accurate as possible, using whatever means were available.

#### 3.1 Primary Quality Assurance/Quality Control

The primary level of quality assurance (QA)/QC for Gv1.1 was the assignment of quality flags to all measured parameters. We used the WOCE flag values defined in Joyce et al (1994). A general description of this procedure and GLODAP modifications is given in Key et al. (2004, Appendix A). Quality flags for all carbon measurements in Gv1.1 were assigned by GLODAP members. In short, a quality flag of 2 means good value, 3 is questionable, 4 is bad value, 6 is an average of replicates, and 9 is sample not collected. The QC flag value “0” did not exist in the original WOCE definitions. It was suggested by GLODAP and subsequently adopted by the WOCE Hydrographic Program (WHP). A flag value of “0” indicates a “good” value that could have been measured but was somehow calculated. For example, large-volume samples collected for radiocarbon analysis on U.S. cruises never had oxygen measurements. Oxygen (and nutrients) were estimated for these bottles by interpolation and were flagged “0.” Unfortunately, we were not always consistent in our treatment of calculated TALK values in Gv1.1, and some calculated TALK values were flagged as “2.” For almost all applications, this error is inconsequential, and it will be corrected in future releases. In the interim, one can identify cruises for which TALK values were calculated from other carbon measurements by referring to Tables 3–5.

During the cruise merge procedure, the QC flags of the GLODAP bottle data were simplified to the subset values 0, 2, and 9 by eliminating values flagged 3 and 4, changing 6 to 2, changing 5 (not reported) to 9 (not collected), and changing the rare occurrence of 7 (manual peak measurements) or 8 (irregular peak integration) to 2 or 9 as appropriate. In general, the primary QA/QC involved assessments that could be made using just the data from that cruise. The GLODAP synthesis effort, however, provided the ability to conduct a second level of QA. These secondary evaluations compared each data set with all the other data sets in that vicinity as described in the following sections.

#### 3.2 Secondary Evaluation of Basic Hydrographic Data

When we began our synthesis in the Indian Ocean, we were unaware of any ongoing efforts to fully calibrate salinity, oxygen, and nutrient data from WOCE-era and earlier cruises. Consequently, when we developed the “crossover” technique described below for carbon, the same technique was applied to the hydrographic data. Results of this effort are available at CDIAC (<http://cdiac.esd.ornl.gov/oceans/glodap/crossover.html>), but were not used for Gv1.1. The initial procedure we developed proved to be too labor-intensive for our small group; the additive correction was not ideal for nutrients; and, most important, we learned of independent objective efforts to accomplish this task. For Gv1.1 we adopted the hydrographic corrections from Gouretski and Janke (2001) for the Atlantic. For the Pacific WOCE-era cruises, we used salinity and oxygen corrections from Johnson et al. (2001) and the unpublished results from C. Mordy, L. Gordon, G. Johnson, and A. Ross for the nutrients. Historic Pacific cruise hydrographic adjustments from Gouretski and Janke (2001) were used. For the Indian Ocean, the hydrographic adjustments were more complicated because no one included all the cruises in an analysis. For the main U.S. WOCE survey cruises (I1–I10, S4I), we used salinity corrections from Johnson et al. (2001), oxygen corrections from Gouretski and Janke (2001), and nutrient corrections from the unpublished work of C. Mordy, L. Gordon, G. Johnson, and A. Ross. For the remainder of the WOCE-era cruises and the historic cruises, all hydrographic adjustments were from Gouretski and Janke (2001).

The procedure we used is far from ideal. Fortunately, most of the adjustments to salinity, oxygen, and nutrients were small. In the future, we will either adopt the semi-automated procedure of Johnson et al.

(2001) or omit hydrographic adjustments. We are aware of one error we made during this process. The final report for Atlantic cruise OACES93 (A16N, Atlantic cruise number 23; Castle et al. 1998) suggested an oxygen correction of +7.5  $\mu\text{mol/kg}$ , which we made to our master data file for this cruise. During the merge procedure, the corrections derived by Gouretski and Janke (2001) were also applied (see Table 10), so the oxygen data were “double corrected.” This value will be corrected in future releases; but in the interim, we recommend that 7.5  $\mu\text{mol/kg}$  be subtracted from all oxygen values for this cruise.

The secondary calibration adjustments (all parameters) applied to Gv1.1 are summarized in Tables 8, 9, and 10. In these tables, a blank indicates that the cruise parameter was *not* included in any of the secondary QC procedures. A value of zero indicates that the measurement was considered in a secondary QC procedure but that no adjustment was deemed necessary. A value of “NA” indicates that either the primary or the secondary QC procedure showed the data to be too problematic for inclusion in Gv1.1, and the values were discarded. Footnotes to these tables indicate the adjustment source and whether the value is additive or multiplicative.

### 3.3 Secondary Evaluation of Carbon Parameters

The three ocean syntheses took nearly five years to compile and evaluate. The evaluation procedures evolved over time, since each basin had its own set of issues and our understanding of the data quality assessment procedures improved over time. The synthesis effort included significant input and discussion from all of the PIs involved in this project. Since the certified reference materials (CRMs) were introduced after this program had started, and it was several years before they were routinely used, most of the data evaluation required some level of subjective evaluation. We worked with the data measurement PIs to resolve any discrepancies that were identified. In cases where a clear cause for the problem was identified, we worked with the original PI to update the final cruise data submitted to the data centers. In cases where the evidence suggested a problem with the initial data but no obvious analytical problem could be identified, a group decision to either adjust or reject the data was made. These decisions were limited to the merged data sets generated here and do not affect the individual data files at the data centers.

#### 3.3.1 Evaluation Criteria

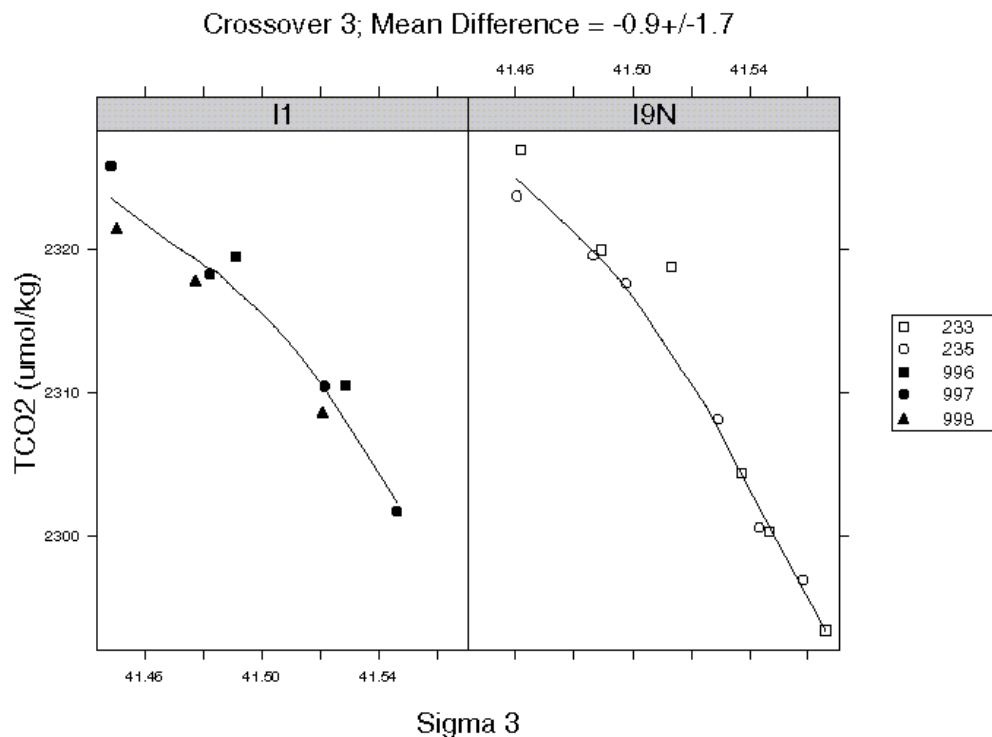
The carbon data quality was assessed using a variety of approaches, as summarized in this section. The details of the approaches are discussed in Sabine et al. (1999), Lamb et al. (2002), and Wanninkhof et al. (2003) for the Indian, Pacific, and Atlantic oceans, respectively.

- **Results of shipboard analysis of CRMs.** CRMs were used on many of the cruises as secondary standards for  $\text{TCO}_2$ , with some exceptions during the Pacific and Atlantic surveys (See Table 2 in Lamb et al. 2002, reprinted as Appendix C, and Wanninkhof et al. 2003, reprinted as Appendix D). Routine analysis of shipboard CRMs helped verify the accuracy of sample measurements. Certification of CRMs for  $\text{TCO}_2$  is based on vacuum extraction/manometric analysis of samples in the laboratory of C. D. Keeling at Scripps Institution of Oceanography (SIO). A complete discussion of the technique developed for CRMs can be found at <http://andrew.ucsd.edu/co2qc/>. Most groups that routinely ran CRM samples for  $\text{TCO}_2$  also analyzed the samples for TALK. The CRMs were certified for TALK in July 1996. However, archived CRMs produced prior to 1996 were calibrated subsequently so post-cruise TALK adjustments could be made. (See Table 3 in Lamb et al. 2002, Appendix C, and Wanninkhof et al. 2003, Appendix D.) CRMs are not available for the other carbon parameters. The measurements made on the earlier CRMs for TALK by the Millero group agreed with the later measurements by Dickson to  $\pm 2 \mu\text{mol/kg}$ .
- **Replicate samples.** Replicate samples were routinely collected and analyzed at sea, thus allowing the analyst to determine the overall measurement precision. Replicate differences include the errors associated with the collection and handling of the carbon sample, as well as the analytical errors. In



addition, replicate samples for TCO<sub>2</sub> were collected at the surface and at 3000 m on select stations along most of the U.S. survey cruises. These samples were shipped to C. D. Keeling's laboratory at SIO for analysis on the mercury manometer (Guenther et al. 1994). Keeling's analyses provided a common point to evaluate cruise-to-cruise differences.

- **Consistency of deep carbon data at the locations where cruises cross or overlap.** One approach for evaluating the consistency of the cruises was to compare data where cruises crossed or overlapped. A location was considered a crossover if stations from two cruises were within 1° (~100 km) of each other. If more than one station from a particular cruise fell within that limit, the data were combined. Only deep-water measurements (>2000 m for the Pacific Ocean, >2500 m for the Indian Ocean, and >1500 m for the Atlantic Ocean) were considered, because CO<sub>2</sub> concentrations in shallow water are variable, and the penetration of anthropogenic CO<sub>2</sub> can change relationships between the carbon parameters measured at different times. Data from the chosen station(s) for each cruise were plotted against potential density referenced to 3000 dB (or 4000 dB in the Atlantic) and fit with a smooth function ("robust loess" function for Indian Ocean and second-order polynomial for the Pacific and Atlantic oceans). Each of the two fitted curves was evaluated at evenly spaced intervals (50 intervals for Indian Ocean and 10 intervals for Pacific and Atlantic) covering the potential density space common to the data from both legs. Then a mean and standard deviation of the point estimates were calculated. Figure 2 shows a typical crossover evaluation.
- **Multiple Linear Regression Analysis.** Another approach used to evaluate the data at the crossover locations was a multiparameter linear regression (MLR) analysis. Brewer et al. (1995) and subsequently others (Wallace 1995; Slansky et al. 1997; Goyet and Davis 1997; Sabine et al. 1999) have shown that both TCO<sub>2</sub> and TALK concentrations in deep and bottom waters can be fit well with MLR functions using commonly measured hydrographic quantities for the independent parameters. The geographic extent over which any such function is applicable depends on the number of water masses present and the uniformity of chemical and biological processes that have affected the carbon species concentrations in different water masses. The MLR coefficients are derived using one data set and then applied to a second to predict TCO<sub>2</sub> or TALK concentrations. The predicted values for the second data set are compared with the measured results for the second data set.
- **Basin-wide MLR Analysis.** As an additional check on the quality of the North Pacific data, the deep (> 2500 m) TCO<sub>2</sub> and TALK data from all of the North Pacific lines north of 20°N were fit with an MLR function of common hydrographic parameters. Relative to the rest of the ocean, the deep North Pacific is extremely uniform in almost all properties and is therefore an ideal region in which to apply a basin-wide analysis. The MLR residuals were investigated for systematic differences between the various cruises. This was particularly useful in the North Pacific, as there were relatively few zonal lines with good-quality data to evaluate crossovers.



**Fig. 2.** A typical crossover plot for the Indian Ocean sections.

- Isopycnal Analysis.** At a few locations in the North Pacific, the crossover offsets were inconsistent with the basin-wide MLR offsets. To determine whether the limited number of stations analyzed biased the crossover results, we expanded the crossover analysis to include additional stations along each cruise and/or stations from neighboring cruises. The deep ( $>2200$  m) station data were averaged at specific potential density ( $\sigma$ -3) values and fitted with a second-order polynomial function. The average differences and standard deviations were determined from evenly spaced differences along the curves. The range of values observed for a particular cruise at each isopycnal level indicated whether the stations initially used in the crossover analysis were offset from the surrounding stations. Although more assumptions about oceanographic consistency are necessary, the additional stations used in the isopycnal analysis can provide a better estimate of the difference between cruises because more data points are included in the analysis.
- Internal Consistency of Multiple Carbon Measurements.** An independent approach to evaluating data accuracy is to examine the internal consistency of the  $\text{CO}_2$  system parameters. The  $\text{CO}_2$  system parameters in seawater can be characterized by temperature, salinity, phosphate and silicate, and two of the four measured inorganic carbon parameters:  $\text{TCO}_2$ , TALK,  $f\text{CO}_2$ , or pH. Thus the carbon system is over-determined on cruises where three or more carbon parameters were measured. By comparing estimates using different pairs of carbon measurements, one can evaluate potential offsets. In addition, examination of internal consistency over several cruises lends confidence to the reliability of the equilibrium constants. The constants of Mehrbach et al. (1973) as a refit by Dickson and Millero (1987) were used for this analysis, along with equilibrium constants for other components (e.g., boric acid dissociation, solubility of  $\text{CO}_2$ , water hydrolysis, and phosphoric and silicic acid dissociation) recommended in Millero (1995). This choice was subsequently supported by the

analysis of a large data set (15,300 samples) obtained from all the ocean basins (Lee et al. 2000; Millero et al. 2002). For our internal consistency analysis, TALK was calculated using a combination of either  $\text{TCO}_2$  and  $f\text{CO}_2$ , or  $\text{TCO}_2$  and pH. At the time of the Pacific and Indian calculations, a +0.0047 pH correction appeared to be necessary for carbon system consistency (DeValls and Dickson 1998). This adjustment was used in the Indian and Pacific calculations; but by the time the Atlantic evaluation was under way, several studies had called this adjustment into question, so the original values were used (see discussion in Section 6.3). Subsequent analysis of the Pacific and Indian calculations did not indicate that the presence or absence of this adjustment would have changed the final conclusions of the quality assessments.

### 3.3.2 Final Evaluation of Offsets and Determination of Correction to be Applied

Based on the available information, an assessment was made of the offsets necessary to make the data sets in a basin mutually consistent. Any cruises that showed consistent offsets of a significant magnitude were adjusted before the data were incorporated into the synthesized dataset.

Some important points must be considered in evaluating the various approaches used to examine the data quality of the cruises. First, most of the approaches assume that the deep ocean does not change over the time period of the various cruises. Second, the various approaches have different strengths and weaknesses. Finally, the calculated offsets and associated errors may not be directly comparable. As a result, some level of subjectivity is necessarily a part of the adjustments proposed in this section. We have made every attempt to consider all of the various lines of evidence available. Adjustments were based on a preponderance of evidence and implemented only when we felt an adjustment was clearly necessary.

#### 3.3.2.1 Indian Ocean Assessment

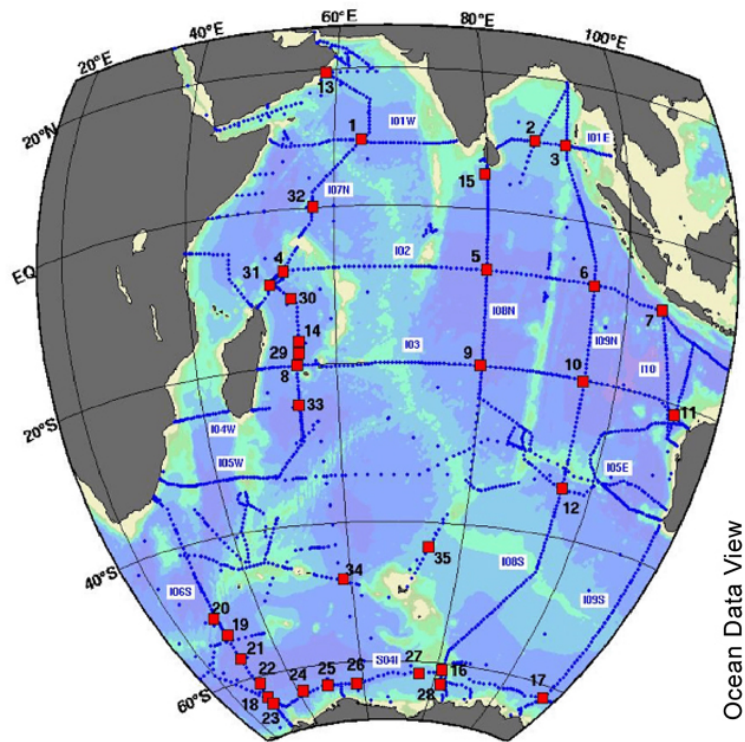
Table 8 lists the final adjustments for Indian Ocean cruises in the Gv1.1 data set. The Indian Ocean assessment was the first to be attempted because we felt that these data had the highest overall initial quality of the WOCE era data.

In an attempt to generate the most consistent carbon data set possible, all of the  $\text{TCO}_2$  and TALK measurements during the 12-leg U.S. WOCE Indian Ocean survey were made using the same equipment. The SOMMA-coulometer systems were provided by D. Wallace's group, and the closed-cell alkalinity systems were provided by F. Millero's group. The scientists running the systems changed with each leg, but the instruments and analytical protocols did not. Furthermore, by 1995, the CRM utility was recognized; and all groups documented their results by analyzing numerous CRMs throughout the cruises. Details of the WOCE/JGOFS Indian Ocean  $\text{CO}_2$  measurement program—including personnel, sampling and measurement protocols, and data QA/QC checks—are provided in Johnson et al. 1998a, Millero et al. 1998, and Johnson et al. 2002a (ORNL/CDIAC-138, NDP-080).

A summary of the combined data set and the details of the evaluation procedure can be found in Sabine et al. (1999; reprinted as Appendix B). The mean and standard deviation of the difference in TALK and  $\text{TCO}_2$  at the 35 intersections identified in Fig. 3 are shown in Fig. 4. Given the thorough calibration and QA of the original cruise data (e.g., Johnson et al. 1998a, Millero et al. 1998, and Johnson et al. 2002a (ORNL/CDIAC-138, NDP-080) and the consistency of the crossover results, we decided additional evaluation approaches were not necessary for this data set.

NOAA carried out a cruise (Gv1.1 Indian cruise number 2, I8R) that repeated a portion of WOCE leg I8N15E between 20° S and 5° N. For the overlap region, a detailed comparison was made. The data in the overlap region from each cruise were individually gridded as a section vs. potential density space. The two gridded sections were then subtracted, the results contoured, and a mean difference calculated. This comparison showed no significant offset between NOAA and DOE data below 2500 dB.

The long-term stability of the WOCE/JGOFS measurements can be estimated from the first 17 crossover results. The mean of the absolute values for the leg-to-leg differences was less than the estimated accuracy for both  $\text{TCO}_2$  ( $1.8 \pm 0.8 \mu\text{mol/kg}$ ) and TALK ( $2.4 \pm 1.6 \mu\text{mol/kg}$ ). Although there is only one reliable crossover point between the WOCE cruises and the CIVA1 cruise (I06S; Gv1.1 Indian Ocean cruise number 12), the differences for both parameters is within the estimated measurement



**Fig. 3. Station locations for Indian Ocean Survey cruises.** Numbered boxes indicate the locations of crossovers discussed in the text.

accuracy. CIVA1 CRM results also support the quality of the measurements. Some of the older INDIGO cruises, however, did appear to have offsets relative to the WOCE and CIVA1 data. INDIGO I and II TALK values averaged  $6.5 \mu\text{mol/kg}$  high and  $6.8 \mu\text{mol/kg}$  low, respectively, while the INDIGO III TALK values showed no clear offset. The INDIGO  $\text{TCO}_2$  values were all consistently high relative to WOCE and CIVA1, with differences of  $10.7$ ,  $9.4$  and  $6.4 \mu\text{mol/kg}$ , respectively. These offsets are consistent with differences observed between at-sea values and replicate samples run at C. D. Keeling's shore-based  $\text{TCO}_2$  facility. Since the INDIGO cruises were run before the introduction of CRMs, these offsets were presumed to be calibration differences; and each leg was adjusted to bring the values in line with the remaining cruises. The dotted boxes in Fig. 4 show the original offsets at the crossovers. The solid boxes show the final offsets for the GLODAP database. The mean of the absolute values for the leg-to-leg differences for all 35 crossover analyses suggests that the final data set is internally consistent to  $2.2$  and  $3.0 \mu\text{mol/kg}$  for  $\text{TCO}_2$  and TALK, respectively.

Cruises I8R and S4I had pH and/or  $\text{pCO}_2$  measurements in addition to  $\text{TCO}_2$  and TALK, but there were no crossovers to evaluate these parameters. Gv1.1 contains neither pH nor  $\text{pCO}_2$  data.



dataset and Table 9 the carbon adjustments that were applied. The details of the Pacific carbon data assessment are given in Lamb et al. (2002, Appendix C).

All of the evaluation approaches listed in Section 3.3.1 were used for the Pacific dataset. Table 11 presents a summary of the TCO<sub>2</sub> quality assessment results. Results of statistical analysis for recommended adjustments of TCO<sub>2</sub> during the Global CO<sub>2</sub> Survey cruises in the Pacific Ocean are presented in Table 12. Our assessment of the Pacific TCO<sub>2</sub> data indicates that the reported values are accurate to ±3 μmol/kg after recommended adjustments of +4, -7, and -4 μmol/kg for legs P16N, P17N, and P2, respectively.

Table 13 is a summary of the TALK quality assessment results. Results of statistical analysis for recommended adjustments of TALK are presented in Table 14. The TALK data are generally good to ±5 μmol/kg after adjustments of +6, -9, -12, +14, and -6 μmol/kg for legs P8S, P17C, P17N, P2, and P31, respectively.

Although significant differences were noted in the *f*CO<sub>2</sub> values depending on the depth of the samples and the system used to analyze them, there is insufficient evidence to propose a correction to any of these data. See further discussion in Section 6.4.

Given the evidence for the need to adjust the spectrophotometric pH values at the time of this synthesis, we recommend adjusting all spectrophotometric pH values upward by 0.0047 to be internally consistent with the other carbon parameters. See Section 6.3 for further discussion of these adjustments. Since pH is not retained in the final dataset, this issue does not impact the Gv1.1 dataset.

### 3.3.2.3 Atlantic Ocean Assessment

The analysis of the Atlantic inorganic carbon data quality is fully described in Wanninkhof et al. (2003, Appendix D). This study followed the procedures outlined in Lamb et al. (2002) with slight modifications to accommodate the circulation and property distribution differences between the Atlantic and the Pacific. The differences are in the technical details as outlined by Wanninkhof et al. (2003) and should not make a difference in the overall conclusions.

Table 5 lists the Atlantic Ocean cruises in Gv1.1 and Table 10 the carbon adjustments that were applied. Based on the overall precision of the measurements on the cruises, we recommended adjustments only if there was clear and consistent evidence for biases of greater than 4 μmol/kg for TCO<sub>2</sub> and 6 μmol/kg for TALK.

In the course of the investigation, we determined that data from several cruises were not suitable for further analysis because of significant scatter in the data. These data are not used in the synthesis and were deleted from Gv1.1

- A06 - TCO<sub>2</sub> and TALK
- A07 - TCO<sub>2</sub> and TALK
- A01E - TALK
- A23 - TCO<sub>2</sub>

No adjustments were recommended for TCO<sub>2</sub>, and the TCO<sub>2</sub> data are believed to be consistent to 4 μmol/kg. We recommended that all TALK data from the A01W section be adjusted upward by 14 μmol/kg and that 7 μmol/kg be subtracted from TALK data from the A09 section. All other TALK data are believed to be consistent to 6 μmol/kg. Subsequent to our work, the PIs for A17 (Gv1.1 Atlantic cruise number 24) compared the TALK data from that cruise with other measurements and suggested that the A17 TALK values be adjusted downward by 8 μmol/kg (Rios et al. 2005). Although significant differences were noted in the *f*CO<sub>2</sub> values, depending on the depth of the samples and the system used to analyze them, there was insufficient evidence to propose a correction to any of these data (see further discussion in Section 6.4). Eleven of the 24 cruises had pH measurements. Different analysis techniques were used, and the pH values were recorded on different reference scales. Metadata provided with the pH measurements often were not sufficient to fully comprehend methods and corrections.

### 3.4 Carbon-14

When WOCE fieldwork began in the early 1990s, the AMS method for analyzing small-volume samples (~500 mL) was not fully operational. Therefore, in the Pacific Ocean, deep waters (1500 m and deeper) were generally sampled using large-volume samples (~250 L). Large-volume water samples were collected using the same Gerard barrels and counted using the same laboratories, equipment, and methods as had been used on previous expeditions such as GEOSECS, TTO, and SAVE. Details of the large-volume procedure have been described in detail previously and are not repeated here (Stuiver et al. 1974; Stuiver and Polach 1977; Key et al. 1994; Key 1996; Stuiver et al. 1996). The AMS procedures are also well described in the literature (McNichol et al. 1994, 2000; Osburn et al. 1994; Schneider et al. 1995; Key et al. 1996; von Reden et al. 1999). A careful error analysis of replicate AMS results from the Pacific WOCE program was conducted by Elder et al. (1998). They concluded that the accuracy of the WOCE AMS measurements was approximately 4‰. A similar comparison for large-volume samples was precluded by the extreme expense of replicate sampling. Numerous tests—such as comparisons of deep-water measurements at the same location and different times, AMS and large-volume measurements from the same depth at the same location and time, and larger-scale consistency checks—lead us to believe that the accuracy of the large-volume results is approximately 4‰. It is important to note that the uncertainty reported for radiocarbon in the WOCE and GLODAP compilations is the laboratory-based error only (primarily counting error).

Because historical data seldom existed, that sort of comparison was limited. For most data, the only sort of comparison possible was a consistency check within each station and within neighboring stations from the same cruise. Very limited larger-scale comparisons with other methods have been tested (see Keller et al. 2002 and Gruber et al. 2000). To date no significant systematic differences have been found between the WOCE data and historical data collected since the 1970s. Therefore, none of the radiocarbon results included in the GLODAP collection have been adjusted in any manner.

### 3.5 Chlorofluorocarbons

Measurements of CFCs on WOCE cruises in the Atlantic, Pacific, and Southern Oceans were made by a number of PIs using different analytical systems and gas standards. For example, CFC measurements during the WHP Pacific Basin one-time survey were made by 8 institutions on more than 27 oceanographic cruises over a 5-year period. In contrast, a single CFC analytical system and set of standards were used on the WOCE Indian Ocean expedition.

Each CFC PI was responsible for working up and calibrating his or her cruise data sets. Before submission to the WHP office, each PI performed an initial data quality evaluation (DQE) on his or her section data and assigned an initial numerical data quality flag (QUALT1) to each CFC-11 and CFC-12 sample.

As part of the WOCE synthesis effort, a second level of DQE was performed on the CFC data sets from each basin. Each basin assessment had a different leader:

Basin	DQE
North Atlantic	Smethie and LeBel
South Atlantic	Roether (pending)
Indian	Fine and Willey
Pacific	Bullister and Wisegarver
Southern	Warner and Min

During these basin evaluations, the CFC data were converted to a common calibration scale (SIO 98). A variety of standard tests were applied to each set of cruise data. For regions where detectable levels of CFCs were present, CFC data from each cruise were examined on a station-by-station basis to check for anomalous CFC concentrations or CFC-11/CFC-12 ratios in vertical profiles and between adjacent stations. These samples were compared with other parameters, including temperature, salinity, and dissolved oxygen to check for correlations with other indices of water mass ventilation processes. The

pCFC-11/pCFC-12 ratios in the water samples (pCFC-11 and pCFC-12 are the partial pressures of CFC-11 and CFC-12) were compared with the atmospheric history of the CFC-11/CFC-12 ratio. Near-surface concentrations were compared with those predicted using the Walker et al. (2000) atmospheric models for CFCs as a function of latitude and time. Previous studies (e.g., Warner et al. 1996) have shown that large regions of the North and Central Pacific were essentially CFC-free in the late 1980s. These deep and homogenous regions provide a check of the sampling and analytical blank levels attainable for CFC analysis on some cruises.

Comparisons were made with CFC data from other cruises in the region, including at crossovers with other WOCE sections. Because of the transient nature of the CFCs, the usefulness of crossover comparisons is more limited for CFCs than for many other WOCE parameters, such as temperature, salinity, oxygen, and nutrients. Based on these checks, a second DQE flag (QUALT2) was assigned to each CFC measurement.

For a small number of cruises, the estimated overall accuracy of the CFC measurements fell slightly outside the original WOCE guidelines ( $\sim 0.005$  pmol/kg, or 1%, whichever is greater). For these cruises, a “relaxed” standard of  $\sim 0.015$  pmol/kg or  $\sim 3\%$  was used in assigning QUALT2 flags to the data. After this secondary DQE process, the CFC data along with both DQE flags were returned to the data originator. In almost all cases, the data originators agreed with the DQE-assigned QUALT2 flags, and the QUALT1 flags were then revised to agree with the QUALT2 flag values. Documentation files containing detailed information on CFC analytical procedures and problems, standards and calibration scales, and blank corrections applied to the data are available at: <http://whpo.ucsd.edu>



## 4. DERIVED VALUES

The derived quantities potential alkalinity (PALK), bomb  $^{14}\text{C}$ , natural  $^{14}\text{C}$ ,  $^{14}\text{C}$  age, CFC partial pressures, CFC age, and anthropogenic  $\text{CO}_2$  are included in Gv1.1 datasets. Except for anthropogenic  $\text{CO}_2$ , these calculations are routine and were done with individual computer routines after the data files had been merged and calibrated. Initial flag values were assigned as part of the calculation. The initial flag values were set to equal the highest (worst) flag of the various parameters used in the calculation. All calculated values were subsequently subjected to the same initial QC procedure used for measured parameters. Calculated parameters with a flag value of 3 or 4 were subsequently deleted from the data set. Summary totals for the remaining PALK, bomb  $^{14}\text{C}$ , and anthropogenic  $\text{CO}_2$  values are given in Table 15. Summary totals for calculated CFC parameters (pCFC and CFC age) are similar to the measurement totals listed in Table 6. Specifics for each calculation are given below.

### 4.1 Anthropogenic $\text{CO}_2$

Anthropogenic  $\text{CO}_2$  estimates have been made on a subset of the GLODAP dataset using the  $\Delta\text{C}^*$  technique first described by Gruber et al. (1996). The calculations were made for the Indian (Sabine et al. 1999), Pacific (Sabine et al. 2002a), and Atlantic (Lee et al. 2003) oceans individually as the data sets were compiled and evaluated as described earlier. The specific techniques used to estimate the anthropogenic  $\text{CO}_2$  have been well described in the three papers presenting these results. This discussion assumes that the reader is familiar with the details in these papers and focuses on the differences between the three basin analyses.

The Indian Ocean was the first WOCE era ocean dataset to be evaluated using the  $\Delta\text{C}^*$  technique (Sabine et al. 1999). The approach used was very similar to the techniques of Gruber et al. (1996) and Gruber (1998). The primary differences were the addition of a denitrification correction to the basic  $\Delta\text{C}^*$  calculation and the derivation of a new preformed alkalinity (Alk0) term. The denitrification term was necessary to account for the differing carbon-to-oxygen ratios in regions of significant denitrification, such as the Arabian Sea. The revised Alk0 term was generated because the original Alk0 equation was produced with data that had not gone through the same QC steps as the Indian Ocean data set and was somewhat Atlantic-biased in its data distribution.

The Pacific analysis was conducted immediately after the Indian Ocean analysis (Sabine et al. 2002b). The water mass distributions in the Pacific were sufficiently complicated that we decided to employ an optimum multiparameter (OMP) analysis for the evaluation of the air-sea disequilibrium term ( $\Delta\text{C}^{\text{diseq}}$ ). For shallow or ventilated isopycnal surfaces that contain measurable levels of CFCs, the  $\Delta\text{C}^{\text{diseq}}$  terms for the water sources were derived from the CFC-12 corrected  $\Delta\text{C}^*$  calculation ( $\Delta\text{C}^*_{12}$ ) on a range of isopycnal surfaces. For isopycnal surfaces located in the interior of the ocean where CFC-12 is absent and where one can reasonably assume that there is no anthropogenic  $\text{CO}_2$ , the  $\Delta\text{C}^*$  values in these waters are equal to  $\Delta\text{C}^{\text{diseq}}$ . To ensure that the  $\Delta\text{C}^{\text{diseq}}$  values for deep density surfaces were not contaminated with anthropogenic  $\text{CO}_2$ , we used only  $\Delta\text{C}^*$  values showing no obvious trend along the isopycnal surface. In the Indian Ocean,  $\Delta\text{C}^{\text{diseq}}$  was evaluated assuming contributions were only from a northern or southern end member. The two end member case can be explicitly solved for each surface using a conservative tracer such as salinity. Upon analyzing the Pacific dataset, it became clear that a two end member mixing was not sufficient. The multiparameter analysis was introduced by Tomczak (1981) by adding oxygen and nutrients as additional quasi-conservative parameters, assuming that biogeochemical changes were negligible. The OMP technique evolved over the next two decades to account for the non-conservative behavior of biological parameters using stoichiometric ratios, allowing for improved determinations of mixing coefficients for multiple water-types (e.g., Tomczak and Large 1989; You and Tomczak 1993; Karstensen and Tomczak 1998; Pérez et al. 2001). The OMP approach used in the Pacific analysis allowed us to de-convolve up to five end members on each isopycnal surface.

In addition to the improved mixing analysis, the Alk0 equation was revised using the Pacific surface alkalinity data. Both the original Gruber et al. (1996) and the Indian Ocean (Sabine et al. 1999) equations

overestimated the alkalinity at low values and underestimated at higher values. A new equation was derived using all of the Pacific alkalinity data shallower than 60 m (~1900 data points). The form of the equation was the same as that used by Sabine et al. (1999).

The Atlantic  $\Delta C^*$  calculations were performed by Lee et al. (2003). Like the Pacific analysis, these calculations used an OMP approach to evaluate the mixing on isopycnal surfaces. An Atlantic Alk0 term was derived with the WOCE-era data. The Indian and Pacific Alk0 calculations were based on a multiple linear regression of temperature, salinity, and phosphate for the upper 60 m. In a similar manner, the Atlantic Alk0 function was derived by fitting alkalinity data from the upper 100 m as a function of temperature, salinity, and nitrate. The most significant difference between the Atlantic analysis and the other oceans was the way the upper ocean was evaluated. In the Pacific and the Indian oceans, the anthropogenic  $CO_2$  in the upper 150 m was evaluated by subtracting  $\Delta C^*$  from  $\Delta C^*_{t12}$  at each bottle rather than attempting to evaluate mean values on isopycnal surfaces. Thus the instantaneous CFC-12 age from each bottle was used to estimate the anthropogenic signal. This approach did not yield satisfactory results in the Atlantic analysis; so instead, the  $\Delta C^*_t$  values in the upper 100 m were calculated assuming an age of zero. Although this is a subtle difference, the net result would be an estimation of higher anthropogenic values in the near-surface waters. The higher Atlantic Ocean surface water anthropogenic  $CO_2$  estimates are obvious in the Gv1.1 map but are minor with respect to the global inventory.

Although there were slight differences in the details of the techniques used to estimate the anthropogenic  $CO_2$  in the different oceans, we believe that these estimates are all comparable and can be combined to generate a global estimate of anthropogenic  $CO_2$  in the ocean. Details of the global synthesis were presented by Sabine et al. (2004, Appendix E) and are briefly reviewed in Section 5.3.

#### **4.2 Potential Alkalinity**

Potential Alkalinity [PALK = (alkalinity +  $NO_3$ )/salinity\*35] corrects TALK for the effects of mixing and the small changes resulting from the decomposition of organic matter, leaving only the influence of calcium carbonate dissolution (Brewer and Goldman 1976). Rubin and Key (2002) have noted that there is a very strong linear relationship between the increase in potential alkalinity and natural  $^{14}C$  decay in the deep ocean, making this a useful tracer for deep-ocean circulation and for isolating bomb  $^{14}C$  (Fig. 5).

#### **4.3 Bomb and Natural Carbon-14**

In addition to the measured radiocarbon values, the GLODAP compilation also tabulates estimates of the bomb-produced and natural (pre-bomb)  $^{14}C$  components. Wherever potential alkalinity values exist, the separation into components was done using the method of Rubin and Key (2002). When potential alkalinity data were not available, the components were estimated using the silicate method described by Broecker et al. (1995) with the additional calibration step and latitude constraint used by Rubin and Key (2002).

#### **4.4 pCFC and CFC ages**

The partial pressure of dissolved CFC in a water sample (pCFC) is calculated by dividing the measured CFC concentration by the solubility coefficient for the CFC, which is a simple function of the temperature and salinity of the sample (Warner and Weiss 1985). To determine the pCFC apparent age of the water sample, the pCFC of the water sample is compared with the atmospheric CFC source function to determine the date at which water with the observed pCFC would have been in equilibrium with the atmospheric CFC concentration. The pCFC apparent age is the elapsed time from that date to the date of the CFC measurement.

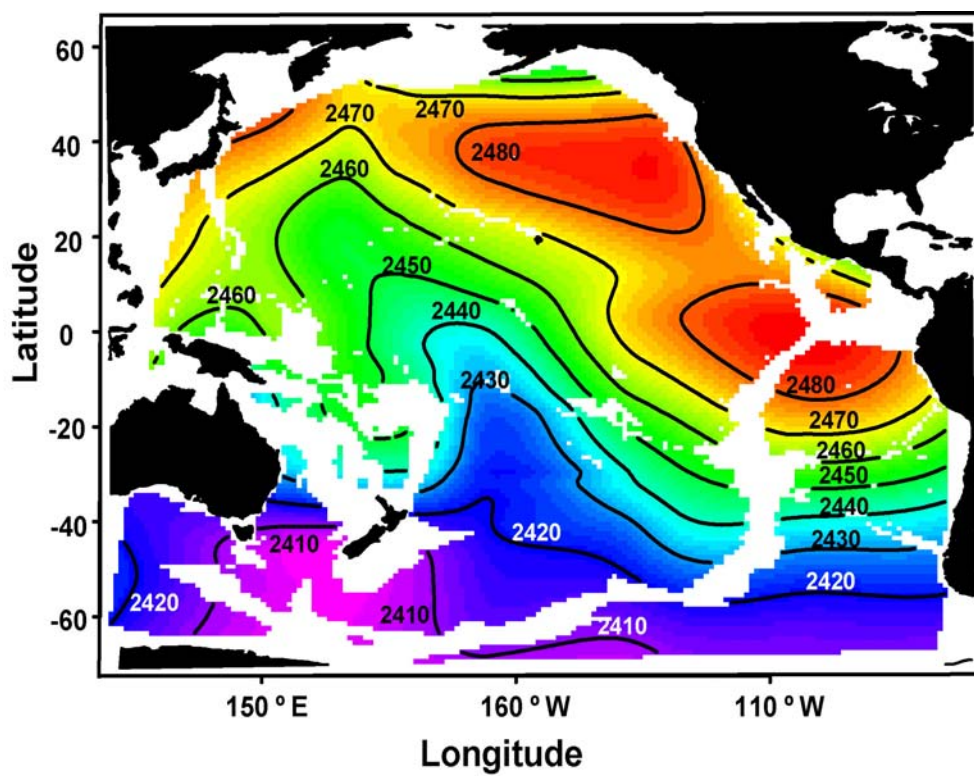


Fig. 5. Map of the potential alkalinity in the Pacific Ocean bottom waters.



## 5. GRIDDED PRODUCTS

GLODAP has produced a calibrated, uniform data set that is the largest compilation of its kind to date. These data were used to produce objectively mapped 3-dimensional fields for the primary GLODAP fields where high-quality climatologies do not exist. For complete details on GLODAP data set construction and mapping procedures, refer to Key et al. (2004, Appendix A).

### 5.1 Included Parameters

The list of mapped parameters includes:

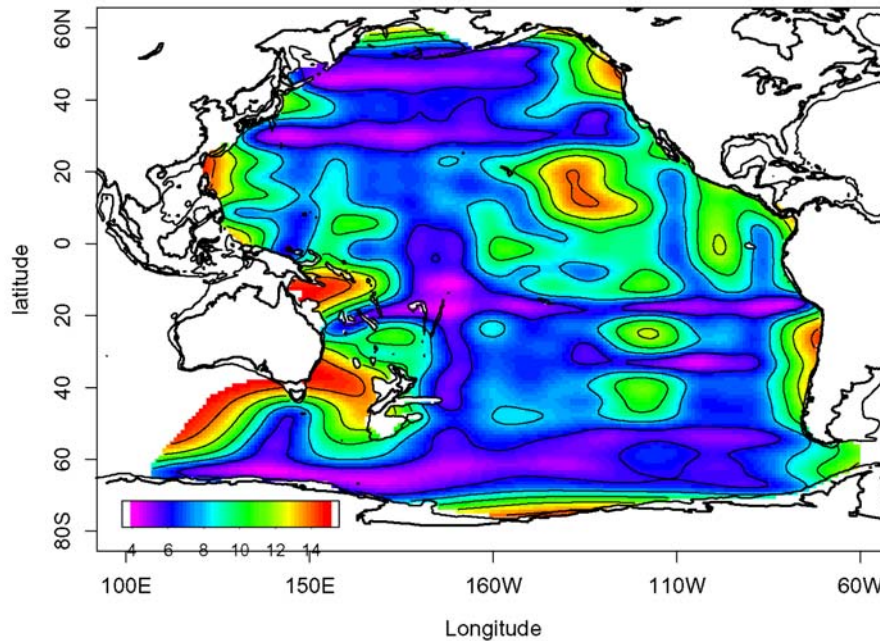
- Total alkalinity ( $\mu\text{mol/kg}$ )
- Potential alkalinity ( $\mu\text{mol/kg}$ )
- Total carbon dioxide ( $\mu\text{mol/kg}$ )
- Anthropogenic  $\text{CO}_2$  ( $\mu\text{mol/kg}$ )
- $\Delta^{14}\text{C}$  (‰)
- Bomb-produced  $\Delta^{14}\text{C}$  (‰)
- Natural (background or pre-bomb)  $\Delta^{14}\text{C}$  (‰)
- CFC-11 (pmol/kg)
- pCFC-11 (patm)
- CFC-12 (pmol/kg)
- pCFC-12 (patm)

For  $\text{TCO}_2$  and CFCs, only WOCE-era data were used for surfaces extending from 0 through 1200 m. For the deeper  $\text{TCO}_2$  and CFC maps and for all of the TALK and potential alkalinity maps, the entire data set was used. No attempt was made to adjust the anthropogenically influenced parameters to a single date. We believe that these adjustments would produce errors approximately equal to those incurred by ignoring the temporal differences/changes over a 10-year time span. Working independently with the WOCE CFC data, Willey et al. (2004) reached the same conclusion. The radiocarbon maps could not be produced using these rules because of a lack of WOCE-era data in the Atlantic: there were no data in the Northeast Atlantic and only one sparsely sampled cruise in the South Atlantic. Therefore, the Atlantic radiocarbon maps ( $\Delta^{14}\text{C}$  and bomb-produced  $\Delta^{14}\text{C}$ ) were constructed with data from the 1980s (primarily TTO and SAVE) results. The SAVE sampling occurred between November 1987 and March 1989, so the time mismatch with WOCE is small; however, the North Atlantic is approximately a decade out of phase. Additional radiocarbon samples collected in the North Atlantic are currently being analyzed. When these results are final, the radiocarbon maps for the North Atlantic will be updated.

### 5.2 Gridding Procedures

The first step of the mapping procedure was to interpolate the discrete data onto the depth surfaces. For this work, the data at each station were fit with a smooth curve (quasi-Hermitian- piece-wise polynomial) that was then evaluated at 33 surfaces. Each interpolated value was subjected to a “distance to nearest data” criterion. The severity of the rejection criterion relaxed with depth. The horizontal mapping resolution was  $1^\circ$  (latitude  $\times$  longitude). Both the horizontal grid box edges and the depth surfaces were chosen to match existing climatological data sets (Conkright et al. 2002 and its predecessors). The horizontal gridding of the discrete data used the “objective analysis” procedure described by Sarmiento et al. (1982) that was based on the work of Gandin (1963). Other than the error estimation, the procedure is very similar to that described by LeTraon (1990).

Primarily because of computer limitations, the Atlantic, Indian, and Pacific were mapped independently. At high southern latitudes, each ocean was “extended” both eastward and westward to facilitate subsequent merging into a global map (see Figure 6 for an example of the extension used in the Pacific maps). A fourth set of maps was produced covering the entire Southern Ocean with the wintertime

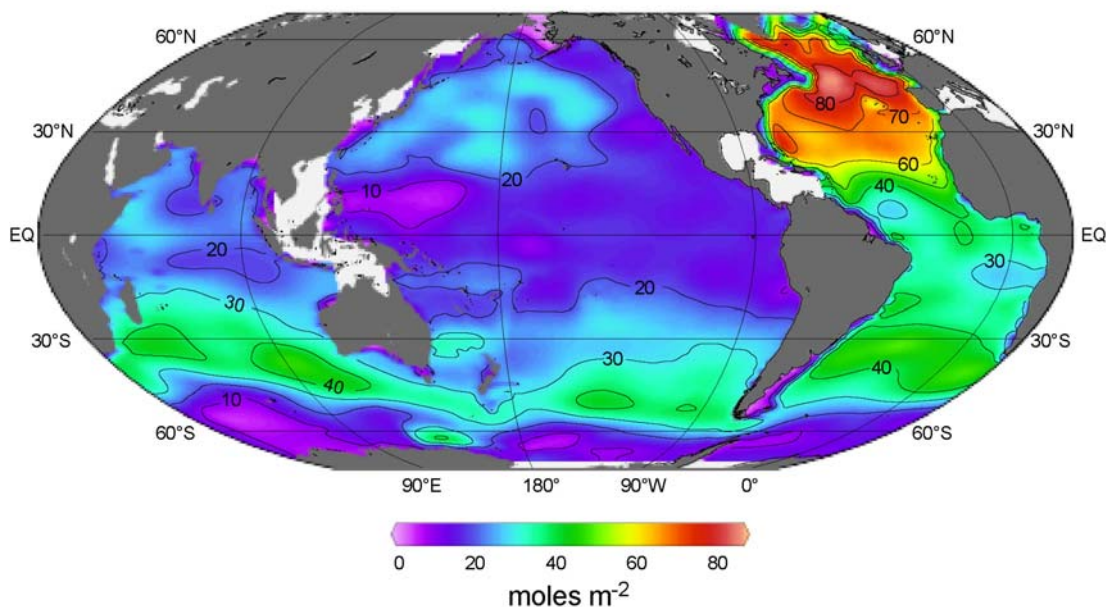


**Fig. 6. Pacific Ocean map showing an extension of gridded alkalinity error fields into the Indian and Atlantic Oceans.**

surface outcrop of the 17° isotherm used as the northern boundary. Finally, for each property at each surface, the four “ocean” maps were pasted together to yield a global picture. For those grid boxes where various ocean maps overlapped, the individual grid box values were smoothed by computing an error weighted average and standard error. An exception to these rules was used for the radiocarbon bomb-radiocarbon maps. For these tracers, the data set was small enough that the entire global ocean could be mapped at once for each surface. Since the global survey had limited data coverage in the marginal basins (the South China Sea/Indonesian region, Yellow Sea, Japan/East Sea, Sea of Okhotsk, Gulf of Mexico, North Sea, Mediterranean Sea, and Red Sea) and the Arctic Ocean (north of 65°N), these areas were excluded from the mapped regions.

### 5.3 Anthropogenic CO<sub>2</sub> Inventory

Sabine et al. (2004) have estimated the total inventory of anthropogenic CO<sub>2</sub> over the mapped regions to be 106 PgC for a nominal year of 1994 (Figure 7). This value was determined by first setting the negative values in the gridded anthropogenic CO<sub>2</sub> files to zero, converting the mass units to volume units using density calculated from the Levitus temperature and salinity fields, multiplying the anthropogenic concentration by the volume of each box based on a one-degree resolution bottom topography, then summing up the carbon in all the boxes.



**Fig. 7. Column inventory of anthropogenic CO<sub>2</sub> estimated by Sabine et al. (2004).**

Note that although negative anthropogenic CO<sub>2</sub> values are not physically possible, we decided to leave these values in to give the user a better understanding of the variability in the final gridded product. The uncertainty in the total inventory is estimated to be approximately 16%, based on uncertainties in the anthropogenic CO<sub>2</sub> estimates and mapping errors. Uncertainties in the former arise from both random errors and potential biases. The random errors, including the precision of the original measurements, have been estimated to be about  $\pm 8 \mu\text{mol/kg}$  (Gruber et al. 1996; Sabine et al. 1999; Sabine et al. 2002a; Lee et al. 2003; Gruber 1998). This estimate is about twice as large as the standard deviation of the  $\Delta C^*$  values below the deepest anthropogenic CO<sub>2</sub> penetration depth, suggesting that the propagated errors may be a maximum estimate of the random variability. Based on these estimates, the limit of detection for this technique is assumed to be  $\sim 5 \mu\text{mol/kg}$ . The impact of these random errors on the uncertainty of the inventory is negligible, as a large number of samples were averaged to estimate the inventory.

The potential biases in the technique are much more difficult to evaluate and could include errors in the (1) biological correction resulting from the assumed stoichiometric relationships; (2) water mass age estimates based on CFCs; (3) assumption of minimal diapycnal mixing; (4) assumption that oxygen was in equilibrium in surface waters; and (5) assumption that the air-sea disequilibrium term is constant over time. Biases in the technique have been evaluated primarily with sensitivity studies and comparisons with other approaches (e.g., Gruber et al. 1996; Sabine et al. 1999; Sabine et al. 2002a; Lee et al. 2003; Gruber et al. 1998; Wanninkhof et al. 1999; Coatanoan et al. 2001; Sabine and Feely 2001). These studies estimated the potential biases to be about 10–15%. The mapping errors can be estimated from the objective mapping calculations (Sarmiento et al. 1982) but are also difficult to assess quantitatively since the mapping errors are highly correlated both vertically and horizontally (Key et al. 2004). We assume that their contribution is  $\sim 15\%$ .

To arrive at a full global ocean inventory, Sabine et al. (2004) assume that the inventory in the unmapped regions south of  $65^\circ\text{N}$  (the marginal basins) scales with ocean surface area. This adds about 6 Pg C to the total. Including the Arctic Ocean (defined here as all ocean north of  $65^\circ\text{N}$ ), using an area scaling approach would increase the total by about 3–4% to 116.5 Pg C. Willey et al. (2004) found that the Arctic Ocean accounted for approximately 5% of the global ocean CFC inventory in 1994. Given the correlation between CFC and anthropogenic CO<sub>2</sub> inventories (McNeil et al. 2003), we adopted the scaling based on CFC inventories for the Arctic Ocean and arrive at a final global anthropogenic CO<sub>2</sub> inventory

estimate of  $118 \pm 19$  Pg C. This inventory pertains to a nominal year of 1994, approximately the median year of our oceanographic measurements.



## 6. LESSONS LEARNED

### 6.1 Importance of CRMs

In compiling the GLODAP dataset and conducting the basin-scale quality assessment, the single most useful source of information about data quality was the CRMs. The mean of a series of CRM analyses conducted over the course of a cruise provides a direct link to the manometric standard for  $\text{TCO}_2$  and a critical tool for comparison to other cruises where CRMs were also run. It can also provide a useful comparison if multiple instruments are run on a cruise. The standard deviation of the mean CRM results provides an assessment of the long-term stability and precision of the instrument(s). Examination of at least daily CRM analyses can provide a good record of the consistency of the measurements throughout the cruise and identify when potential offsets might have occurred. The CRMs are intended as a secondary standard to validate the accuracy of the primary calibration; but in the event of a catastrophic failure in the calibration system, the CRMs, together with a good history of CRM analyses on that instrument when the calibration system was working, may provide a way of manually calibrating the instrument.

We recommend that all investigators making inorganic carbon measurements in the ocean regularly (at least daily) include CRMs in their analysis schedule. A table of the individual CRM results and when they were analyzed (or at the very least, the mean and standard deviation of the CRM results) should be included along with the batch number as part of the meta-data reported with the data. The meta-data also need to clearly state whether the data were adjusted for any offset between the CRM results and the certified value. If multiple instruments were used on a cruise, there should be separate CRM results for each instrument included in the meta-data.

### 6.2 Preferred Thermodynamic Constants

A number of scientists have recently shown that the thermodynamic constants for the dissociation of carbonic acid in seawater of Mehrbach et al. (1973) are more reliable than measurements made on artificial seawater. These studies have largely been confined to looking at the internal consistency of measurements of TALK,  $\text{TCO}_2$ , and  $f\text{CO}_2$ . As part of this work, we have examined the field measurements of pH,  $f\text{CO}_2$ ,  $\text{TCO}_2$ , and TALK on surface and deep waters from the Atlantic, Indian, Southern, and Pacific Oceans to determine the  $\text{pK}_1$ ,  $\text{pK}_2$ , and  $\text{pK}_2 - \text{pK}_1$ . These calculations are possible as a result of the high precision and accuracy of the field measurements. The results of this work were published by Millero et al. (2002). The values of  $\text{pK}_2$  and  $\text{pK}_2 - \text{pK}_1$  over a wide range of temperatures ( $-1.6$  to  $38^\circ\text{C}$ ) were in good agreement (within  $\pm 0.005$ ) with the results of Mehrbach et al. (1973). The measured values of  $\text{pK}_1$  at 4 and  $20^\circ\text{C}$  were in reasonable agreement (within  $\pm 0.01$ ) with all the constants determined in laboratory studies. The Millero et al. (2002) results indicate, as suggested by internal consistency tests, that the directly measured values of  $\text{pK}_1 + \text{pK}_2$  of Mehrbach et al. (1973) on real seawater are more reliable than the values determined for artificial seawater. It also indicates that the large differences of  $\text{pK}_2 - \text{pK}_1$  (0.05 at  $20^\circ\text{C}$ ) in seawater and artificial seawater determined by different investigators are mainly due to differences in  $\text{pK}_2$ . The laboratory studies of Mojica and Millero (2002) have also demonstrated that the Mehrbach et al. (1973) seawater measurements as reformulated by Dickson and Millero (1987) on the seawater scale are more reliable than the measurements in artificial seawater. The differences in artificial seawater and seawater for  $\text{pK}_1$  are within the experimental measurements ( $\sigma = 0.007$ ) of the various studies. The differences in  $\text{pK}_2$  (0.04), however, are larger than the experimental error ( $\sigma = 0.01$ ). At present, we do not know what causes the differences in the  $\text{pK}_2$  between seawater and artificial seawater.

### 6.3 pH Adjustments

Most of the pH measurements during the WOCE era used a spectrophotometric method (Clayton and Byrne 1993), with m-cresol purple as the indicator and either scanning or diode array spectrophotometers. There were some cruises, however, that involved potentiometric measurements with a glass electrode.

Some of the pH values were reported on the total hydrogen scale, while others were reported on the seawater scale. The seawater scale considers the interaction of hydrogen ions with bisulfate and fluoride ions in seawater, while the total scale includes only the bisulfate contribution (Dickson and Riley 1979; Dickson and Millero 1987). The two scales are linked by the following equation:

$$\text{pH}_{\text{SWS}} = \text{pH}_{\text{T}} - \log \left\{ (1 + [\text{SO}_4^{2-}]_{\text{T}} / K_{\text{HSO}_4} + [\text{F}^-]_{\text{T}} / K_{\text{HF}}) / (1 + [\text{SO}_4^{2-}]_{\text{T}} / K_{\text{HSO}_4}) \right\}$$

where  $\text{pH}_{\text{T}}$  is hydrogen ion concentration on the total hydrogen scale,  $[\text{F}^-]_{\text{T}}$  and  $[\text{SO}_4^{2-}]_{\text{T}}$  are the total concentrations of fluoride and sulphate in seawater, and  $K_{\text{HF}}$  and  $K_{\text{HSO}_4}$  are the dissociation constants of hydrogen fluoride and sulphate in seawater (Dickson and Riley 1979).

The limited number of crossovers available for the carbon evaluation study suggested that the spectrophotometric pH measurements were very precise and consistent between cruises. DeValls and Dickson (1998) have suggested, however, that the pH values initially assigned to the tris buffers used to characterize the indicator, m-cresol purple, should be increased by 0.0047. This revision would translate into a comparable increase in the  $\text{pH}_{\text{T}}$  values reported for the spectrophotometric measurements. An upward adjustment in the reported  $\text{pH}_{\text{T}}$  values appeared to be further supported by McElligott et al. (1998) and Lee et al. (2000). As a consequence, we decided to adjust the pH values prior to any calculations for the GLODAP dataset.

Subsequent studies, however, have suggested that this adjustment is not necessary. As demonstrated in the internal consistency study of Millero et al. (2002), the addition of this factor increases the errors in the calculated values. Also, the measurements of spectroscopic and potentiometric pH on seawater made by Mojica and Millero (2002) agree to  $\pm 0.002$  over a wide range of temperature and salinity. Thus we believe that this correction is not needed. The net effect of the pH adjustment on the calculated TALK values in the GLODAP data set (a very small percentage of the dataset) is within the overall uncertainty of the data.

Our recommendation for future groups wishing to make pH measurements is to use the spectrophotometric method at a constant temperature (e.g., 25°C). Data can be reported on either the total or seawater scale, but it is essential when reporting the data to make sure that all necessary meta-data (e.g. pH scale, measured temperature and salinity) are included with the data. There were several data sets that we had to throw out because we did not have the necessary meta-data to figure out what was actually measured.

#### 6.4 Discrete $\text{pCO}_2$ Measurements

Three different types of instruments were used to measure discrete  $f\text{CO}_2$  samples. The system used by Takahashi (Chipman et al. 1993; DOE 1994) involved equilibration of an ~50-mL headspace with an ~500-mL sample at either 4°C (T4 = Takahashi @ 4°C) or 20°C (T20 = Takahashi @ 20°C), depending on ambient surface water temperatures. Note that the Takahashi values, reported as partial pressure of  $\text{CO}_2$  ( $\text{pCO}_2$ ), were converted to  $f\text{CO}_2$  using the correction factor (~0.997) given by Weiss (1974). Wanninkhof and co-workers used two systems during the Pacific Ocean survey cruises. An NDIR-based system (WI20 = Wanninkhof IR @ 20°C) with ~500-mL samples was used for analyses during EQS92 and P18 (Wanninkhof and Thoning 1993). A GC-based system (WG20 = Wanninkhof GC @ 20°C) with samples collected in a closed, septum-sealed bottle having a volume of ~120 mL of seawater and a headspace of ~10 mL was used for P14S15S (Neill et al. 1997).

Detectors were calibrated after every 4 to 12 samples with gas standards traceable to manometrically determined values by C. D. Keeling at SIO. Assessment of  $f\text{CO}_2$  accuracy is difficult because of the lack of aqueous standards. Estimates of precision based on duplicate samples range from 0.1 to 1% depending on  $f\text{CO}_2$  and the measurement procedure, with higher  $f\text{CO}_2$  levels on the WI20 system ( $>700 \mu\text{atm}$ ) giving worse reproducibility (Chen et al. 1995).

All potential crossovers were examined, including crossovers where measured values could be compared with  $f\text{CO}_2$  values calculated from  $\text{TCO}_2/\text{TALK}$  or  $\text{TCO}_2/\text{pH}$  pairs. For the crossover comparison, all samples run at 4°C were normalized to 20°C by calculating the alkalinity (TALK) from

$f\text{CO}_2$  (4°C) and  $\text{TCO}_2$  and subsequently calculating  $f\text{CO}_2$  (20°C) from the  $\text{TCO}_2$  and calculated TALK. The carbonate dissociation constants of Mehrbach et al. (1973) as refit by Dickson and Millero (1987) and ancillary constants listed in DOE (1994) are used for these calculations with the program of Lewis and Wallace (1998).

Analysis of the calculated  $f\text{CO}_2$  values revealed that there may be some problems as a result of uncertainties as to which carbon dissociation constants to use. This is also a problem for the crossovers that required a temperature conversion. For example, the temperature conversion from 4° to 20°C using the Mehrbach constants yields  $f\text{CO}_2$  values for the deep Pacific that are about 50  $\mu\text{atm}$  higher than if the temperature conversion is performed with the Roy constants. Based on the discussions in the previous sections, we recommend that the Mehrbach constants be used to determine the effect of temperature on  $f\text{CO}_2$  and pH.

The standard deviation for the  $f\text{CO}_2$  crossover comparisons in the Pacific was 16.0  $\mu\text{atm}$ . The average of the absolute value of the differences was  $10.3 \pm 13.7$   $\mu\text{atm}$ . Notable offsets were observed for some crossovers in the southern Pacific Ocean, within 15° of each other. If this offset is systematic throughout the cruises, it would imply that the  $f\text{CO}_2$  for S4P and P19 differs by about 30  $\mu\text{atm}$ , which is roughly comparable to an offset of ~4–5  $\mu\text{mol/kg}$  in  $\text{TCO}_2$  or TALK. The largest offsets (35  $\mu\text{atm}$ ) were observed for EQS92. We suspect that this offset was caused by a bias in the analytical system used during this cruise, although biases in the other crossovers involving the infrared (IR) system at 20°C (WI20) were less pronounced. Crossovers where both cruises used the WI20 technique were in excellent agreement. The large headspace-to-water volume of the IR system may be the cause of the error. When  $f\text{CO}_2$  data obtained using the different types of instruments are compared with the calculated  $f\text{CO}_2$  values using TALK and  $\text{TCO}_2$ , a bias between the IR and small-volume GC systems becomes apparent. The GC-based system (WG20) yielded significantly higher  $f\text{CO}_2$  values than calculated values using the recommended constants, while the IR-based system did not show a clear trend, but rather increased scatter with increased  $f\text{CO}_2$ .

Based on careful laboratory studies, it appears that the IR-based measurements may give low results at  $f\text{CO}_2$  values >700  $\mu\text{atm}$ . The deep-water data with WI20 are low by about 20–30  $\mu\text{atm}$  in the range of 1000–1100  $\mu\text{atm}$ . This result is in accordance with the findings of Lee et al. (2000). As suggested by Lee and co-workers, the trend in the calculated values of  $f\text{CO}_2$  from TALK and  $\text{TCO}_2$  most likely results from a thermodynamic inconsistency with the Mehrbach et al. (1973) constants. We recommend that further work be done to understand the potential biases in the  $f\text{CO}_2$  systems. Until this issue is resolved, the large-volume IR-based system appears to be the best choice.

## 6.5 Preferred Measurement Pair for Future Surveys

Based on the discussion in the previous sections, we believe that the ideal measurement pair for future studies is  $\text{TCO}_2$  and TALK. Although both pH and  $f\text{CO}_2$  are potentially more precise measurements than TALK, the issues with accuracy do not make these ideal parameters. Both TALK and  $\text{TCO}_2$  are state variables, so they do not require the large temperature and pressure corrections that are required for pH and  $f\text{CO}_2$ .  $\text{TCO}_2$  and TALK are also an ideal pair because these two parameters are more orthogonal than  $\text{TCO}_2$  and pH or  $f\text{CO}_2$ . Finally, and most important, CRMs exist for TALK and  $\text{TCO}_2$  but not for pH or  $f\text{CO}_2$ .



## 7. ONGOING RESEARCH

Although we have decided to publish the current GLODAP dataset (Gv1.1) to ensure that it is properly documented in the literature, GLODAP will continue to improve and expand the dataset for the foreseeable future. Data assembly continues with the addition of other programs (CARINA, etc.) and other parameters (e.g., Helium/tritium data). We are also trying to assemble data from regions not covered in Gv1.1 (Arctic and marginal seas).

In the next phase of GLODAP, we hope to expand on the 1990s spatial dataset by adding a temporal component. We will be working to collect historical data and evaluate it relative to the WOCE-era data. We will also be working closely with the U.S. CLIVAR/CO<sub>2</sub> repeat hydrography program, CarboOcean, and others to include post-WOCE cruises into the dataset. Please visit the GLODAP web site ([http://cdiac.esd.ornl.gov/oceans/glodap/Glodap\\_home.htm](http://cdiac.esd.ornl.gov/oceans/glodap/Glodap_home.htm)) for future updates.



## 8. HOW TO OBTAIN THE DATA AND DOCUMENTATION

This GLODAP database (NDP-083) is available free of charge from CDIAC. The complete data set and documentation can be obtained in one of the following ways.

**From the CDIAC GLODAP web site:**

[http://cdiac.ornl.gov/oceans/glodap/Glodap\\_home.htm](http://cdiac.ornl.gov/oceans/glodap/Glodap_home.htm)

**Through CDIAC's online ordering system:**

[http://cdiac.ornl.gov/pns/how\\_order.html](http://cdiac.ornl.gov/pns/how_order.html)

**By contacting CDIAC directly:**

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

Telephone: (865) 574-3645  
Telefax: (865) 574-2232  
E-mail: [cdiac@ornl.gov](mailto:cdiac@ornl.gov)  
Internet: <http://cdiac.ornl.gov>





## 9. TABLES

**Table 1. DOE Science Team Members**

<b>Name</b>	<b>Institution</b>
L. Bingler	PNNL
D. W. Chipman	LDEO (retired)
A. G. Dickson	SIO
J. Downing <sup>1</sup>	PNNL
P. R. Guenther	SIO (retired)
C. Goyet	WHOI (now at Universite de Perpignan, France)
K. M. Johnson	BNL (retired)
R. M. Key	PU
C. D. Keeling	SIO (deceased)
A. Kozyr	ORNL, CDIAC
F. J. Millero	RSMAS, University of Miami
C. Olsen	U.S DOE Program Manager (now at University of Massachusetts)
C. L. Sabine	Princeton University (now at NOAA/PMEL)
T. Takahashi	LDEO
D. W. R. Wallace <sup>2</sup>	BNL (now at Univ. of Kiel, Germany)
C. D. Winn	University of Hawaii (now at Hawaii Pacific University)
<b>NOAA members of the Science Team</b>	
R. A. Feely	NOAA/PMEL
R. Wanninkhof	NOAA/AOML

<sup>1</sup>First chairman of the DOE Science Team.

<sup>2</sup>Second chairman of the DOE Science Team.

**Table 2. GLODAP Science Team members and additional contributors**

<b>Name</b>	<b>Institution</b>
<b>GLODAP Science Team members</b>	
J. L. Bullister	NOAA/PMEL
R. A. Feely	NOAA/PMEL
R. M. Key	PU
A. Kozyr	ORNL, CDIAC
K. Lee	Pohang Univ. of Science and Technology, Republic of Korea
F. J. Millero	RSMAS
T.-H. Peng	NOAA/AOML
C. L. Sabine <sup>1</sup>	NOAA/PMEL
R. Wanninkhof	NOAA/AOML
<b>Additional Contributors<sup>2</sup></b>	
R. H. Byrne	University of South Florida
C. D. Choi	Pohang Univ. of Science and Technology, Republic of Korea
S.-N. Chung	Pohang Univ. of Science and Technology, Republic of Korea
S. C. Diggs	SIO/UCSD
G. Eiseheid	WHOI
L.I. Gordon	Oregon State University
D.J. Greeley	NOAA/PMEL
N. Gruber	UCLA
M. Ishii	Meteorological Research Institute, Japan
G. C. Johnson	NOAA/PMEL
M. F. Lamb	NOAA/PMEL (retired)
N. Metzl	Université P. et M. Curie, France
P. Mojica	RSMAS
C. Mordy	NOAA/PMEL
T. Ono	Institute for Global Change Research, Japan
H. G. Östlund	RSMAS
G.-H. Park	Pohang Univ. of Science and Technology, Republic of Korea
D. Pierrot	RSMAS
A. Poisson	Universite Pierre et Marie Curie, France (retired)
D. Purkerson	RSMAS
P. D. Quay	University of Washington
A.F. Rios	Instituto de Investigaciones Marinas, Spain
A.A. Ross	Oregon State University
P. Schlosser	LDEO
M. Stuiver	University of Washington
J. H. Swift	SIO/UCSD
R. G. Schottle	University of Hawaii
B. Tilbrook	CSIRO, Australia
Y.W. Watanabe	National Institute for Resources and Environment, Japan
R. J. Wilke	BNL
C. S. Wong	Institute of Ocean Sciences, Canada

<sup>1</sup>GLODAP Science Team leader;

<sup>2</sup>All members of the DOE Science Team in Table 1 who are not listed as GLODAP Science Team members also are additional contributors to the GLODAP.

Table 3. Indian Ocean cruise summary

Section	No.	EXPOCODE	Ship	Dates	Total	TCO <sub>2</sub>	TALK	CFC	<sup>14</sup> C	Chief Scientist	Carbon	CFC	<sup>14</sup> C
					Stations						Principal Investigator		
WOCE													
16S_b*	1	35MF103_1	<i>M.Dufrense</i>	2/20– 3/22/1996	55 <sup>a</sup>	55	55	54	0	A. Poisson	A. Poisson	A. Poisson	NA
IR04(I8R)*	2	3175MB95_07	<i>M.Baldrige</i>	9/22– 10/25/1995	100 <sup>a</sup>	98	98	95	0	R. Molinari	F. Millero	J. Bullister	NA
SR3S4* <sup>b</sup>	3	AR9404_1	<i>A.Australis</i>	12/13/1994– 2/02/1995	106 <sup>a</sup>	58	58 <sup>a</sup>	79	0 <sup>n</sup>	S. Rintoul	B. Tilbrook	J. Bullister	B. Tilbrook
S04a <sup>c</sup>	4	06AQANTXIII_4	<i>Polarstern</i>	3/17– 5/20/1996	99 <sup>a</sup>	90	0	98	0	E. Fahrbach	M. Hoppema	A. Watson	NA
S05	5	09FA1094	<i>Franklin</i>	11/12– 12/5/1994	68 <sup>a</sup>	0	0	0	0	M. Tomczak	NA	NA	NA
I8A(S04)	6	74DI200_1	<i>Discovery</i>	2/6– 3/18/1993	25 <sup>a</sup>	0 <sup>o</sup>	0	25	0	R. Dickson	J. Robertson	T. Haine M. Krysell M. Liddicoat A. Watson	NA
ISS01_i	7	74DI213_1	<i>Discovery</i>	1/6–2/21/1995	103 <sup>a</sup>	0	0	83	0	R. Pollard	NA	S.Boswell	NA
ISS01_h	8	74DI207	<i>Discovery</i>	2/19– 3/31/1994	32 <sup>p</sup>	0	0	32	0	R. Dickson	NA	R. Dickson	NA
ISS03_b	9	09FA9605	<i>Franklin</i>	5/7–5/31/1996	90 <sup>a</sup>	0	0	0	0	P. McIntosh T.McDougal	NA	NA	NA
IR06_b	10	09FA9508_1	<i>Franklin</i>	9/13– 10/14/1995	104 <sup>a</sup>	0	0	0	0	S. Wijffels	NA	NA	NA
S04I*	11	320696_3	<i>N.B.Palmer</i>	5/3– 7/4/96	108 <sup>a</sup>	108	98	90	31 <sup>e</sup>	J. Swift T.Whitoorth	F. Millero T. Takahashi	W. Smethie M. Wagner	R. Key

Table 3. (continued)

Section	No.	EXPOCODE	Ship	Dates	Total	TCO <sub>2</sub>	TALK	CFC	<sup>14</sup> C	Chief Scientist	Carbon	CFC	<sup>14</sup> C
					Stations						Principal Investigator		
I06S*	12	35MFCIVA_1	<i>M.Dufresne</i>	1/23–3/9/1993	52 <sup>a</sup>	52	52	52	8 <sup>g</sup>	A. Poisson	A. Poisson	A. Poisson	M. Arnold
I08SI09S*	13	316N145_5	<i>Knorr</i>	12/1/1994– 1/19/1995	142 <sup>a</sup>	76 <sup>h</sup>	72 <sup>h</sup>	97	26 <sup>i</sup>	M. McCartney T. Whitworth	D. Wallace	J. Bullister W. Smethie	P. Quay R. Key
I09N*	14	316N145_6	<i>Knorr</i>	1/24–3/5/1995	130 <sup>a</sup>	130 <sup>h</sup>	129 <sup>h</sup>	123	22 <sup>i</sup>	A. Gordon D. Olson	C. Sabine	R. Fine	R. Key
I08NI05E*	15	316N145_7	<i>Knorr</i>	3/10– 4/15/1995	147 <sup>a</sup>	126 <sup>h</sup>	124 <sup>h</sup>	99	20 <sup>i</sup>	L. Talley	C. Winn	W. Smethie	R. Key
I03*	16	316N145_8	<i>Knorr</i>	4/23–6/5/1995	130 <sup>a</sup>	105 <sup>h</sup>	108 <sup>h</sup>	102	20 <sup>i</sup>	W. Nowlin	F. Millero	R. Weiss	R. Key
I05WI04*	17	316N145_9	<i>Knorr</i>	6/11– 7/11/1995	134 <sup>a</sup>	129 <sup>h</sup>	134 <sup>h</sup>	104	15 <sup>i</sup>	J. Toole	D. Wallace	W. Smethie	R. Key
I07N*	18	316N145_10	<i>Knorr</i>	7/15– 8/24/1995	149 <sup>a</sup>	125 <sup>h</sup>	141 <sup>h</sup>	146	22 <sup>i</sup>	D. Olson S. Doney D. Musgrave	C. Winn	R. Fine	R. Key
I01* <sup>q</sup>	19	316N145_11,12	<i>Knorr</i>	8/29– 10/16/1995	153 <sup>a</sup>	149 <sup>h</sup>	149 <sup>h</sup>	149	24 <sup>i</sup>	J. Morrison H. Bryden	C. Goyet	M. Warner	R. Key
I10*	20	316N145_13	<i>Knorr</i>	11/11– 11/28/1995	61 <sup>a</sup>	52 <sup>h</sup>	48 <sup>h</sup>	51	6 <sup>i</sup>	N. Bray	C. Sabine	R. Fine	R. Key
I02* <sup>q</sup>	21	316N145_14	<i>Knorr</i>	12/2/1995– 1/22/1996	168 <sup>a</sup>	161 <sup>h</sup>	166 <sup>h</sup>	153	28 <sup>i</sup>	G. Johnson B. Warren	C. Winn	J. Bullister	R. Key

Table 3. (continued)

Section	No.	EXPOCODE	Ship	Dates	Total	TCO <sub>2</sub>	TALK	CFC	<sup>14</sup> C	Chief Scientist	Carbon	CFC	<sup>14</sup> C
					Stations						Principal Investigator		
<b>Historical</b>													
I05	22	74AB29	<i>C. Darwin</i>	11/12– 12/17/1987	108 <sup>j</sup>	0	0	69 <sup>f</sup>	0	J. Toole B. Warren	NA	R. Fine	NA
INDIGO-1	23	St. 1–25	<i>M. Dufresne</i>	2/24– 3/18/1985	101	101	101	48	33 <sup>k</sup>	A Poisson	A Poisson	A. Poisson	M. Arnold G. Östlund
INDIGO-2		St. 27–69		4/1–4/30/1985						M. Fieux			
INDIGO-3		St. 75–117		1/14– 2/20/1987						N. Metzl			
GEOSECS	24	GEOSECS Leg 3 GEOSECS Leg 4 GEOSECS Leg 5 GEOSECS Leg 6 GEOSECS Leg 7	<i>Melville</i>	12/4/1977– 4/24/1978	51 <sup>l</sup>	42	43	0	40 <sup>m</sup>	R. Williams H. Craig R. Weiss W. Broecker D. Spencer	R. Williams T. Takahashi C. Keeling	NA	G. Östlund M. Stuiver

\*Cruise data used in calculating anthropogenic CO<sub>2</sub>.

<sup>a</sup>Final data report available at WHPO web site.

<sup>b</sup>See listing with Pacific Ocean cruises.

<sup>c</sup>See listings with Atlantic Ocean cruises.

<sup>e</sup>See Key 1999.

<sup>g</sup>See Lebourcher et al. 1999.

<sup>h</sup>See Johnson et al. 2002a.

<sup>i</sup>See Key and Quay, 2002.

<sup>j</sup>See Toole and Warren, 1993.

<sup>k</sup>See Östlund and Grall, 1991; Bard et al. 1988.

<sup>l</sup>See Östlund et al. 1987

<sup>m</sup>See Stuiver and Ostlund 1983.

<sup>n</sup>Not yet measured.

<sup>o</sup>No data on file at WHPO.

<sup>p</sup>See Dickson et al. 1995.

<sup>q</sup>Frequently divided into E and W legs.

<sup>r</sup>See Fine (1993).

Table 4. Pacific Ocean cruise summary

Section	No	EXPOCODE	Ship	Dates	Total	TCO <sub>2</sub>	TALK	CFC	<sup>14</sup> C	Chief Scientist	Carbon	CFC	<sup>14</sup> C
					Stations						Principal Investigator		
<b>WOCE</b>													
P17N <sup>d</sup>	1	31DSCGC91_1	<i>Discoverer</i>	2/16– 2/24/1991	12 <sup>b</sup>	9	0	10	11 <sup>c</sup>	D.Wisegarver	R.Feely	J.Bullister	R.Key
P02*	2	49K6KY9401_1	<i>Kaiyo-Maru</i>	1/8– 2/10/1994	63 <sup>d</sup>	59	57	59	0 <sup>e</sup>	K.Okuda	T.Ono	Y.Watanabe	Y.Watanabe
P06*	3	316N138_3,4,5	<i>Knorr</i>	5/2– 7/30/1992	258 <sup>d</sup>	107 <sup>f</sup>	59 <sup>f</sup>	156	50 <sup>ao</sup>	H.Bryden M.McCartney J.Toole	D.Wallace	R.Fine M.Warner R.Weiss	R.Key
P08S*	4	49XK9605	<i>Kaiyo-Maru</i>	6/17– 7/20/1996	27 <sup>d</sup>	10 <sup>d</sup>	2	0	10 <sup>d</sup>	Yoshioka	Shitashima	NA	Saito
P09*	5	49RY9407_1,2	<i>Ryofu Maru</i>	7/7– 8/25/1994	95 <sup>d</sup>	22	22 <sup>g</sup>	19	10	I.Kaneko S.Kawai	M.Ishii	Tamaki I.Kaneko	Hirose
P10*	6	3250TN026_1	<i>T.Thompson</i>	10/5– 11/10/1993	94 <sup>d</sup>	34 <sup>h</sup>	34 <sup>h</sup>	68 <sup>d</sup>	38 <sup>d</sup>	M.Hall T.Joyce	C.Sabine	M.Warner	R.Key
P13N*	7	31VIC92_0,1,2	<i>J.Vickers</i>	8/4– 10/21/1992	87 <sup>d</sup>	77 <sup>i</sup>	79 <sup>i</sup>	83	41 <sup>d</sup>	J.Bullister B.Taft	A.Dickson C.Keeling	J.Bullister	P.Quay
P14N*	8	325023_1 325024_1	<i>T.Thompson</i>	7/5– 9/2/1993	193 <sup>d</sup>	70	69	135 <sup>d</sup>	0	G.Roden	F.Millero C.Winn	M.Warner R.Gammon	NA
P14S15S*	9	31DSCGC96_1,2	<i>Discoverer</i>	1/5– 3/10/1996	182 <sup>d</sup>	165	157	165	0 <sup>j</sup>	J.Bullister R.Feely	R.Feely F.Millero R.Wanninkhof	J.Bullister	P.Quay
P15N*	10	18DD9403_1,2	<i>J.P.Tulley</i>	9/6– 11/10/1994	122 <sup>d</sup>	69	71	0	0 <sup>k</sup>	J.Garrett H.Freeland	C.S.Wong	C.S.Wong	C.S.Wong
P16S17S*	11	31WTTUNES-2	<i>T.Washington</i>	7/16– 8/25/1991	97 <sup>d</sup>	91 <sup>l</sup>	85 <sup>m</sup>	97 <sup>d</sup>	26 <sup>d</sup>	J.Swift	C.Goyet T.Takahashi	R.Fine	R.Key
P16C*	12	31WTTUNES_3	<i>T.Washington</i>	8/31– 10/1/1991	106 <sup>d</sup>	21 <sup>n</sup>	21 <sup>n</sup>	57 <sup>d</sup>	29 <sup>d</sup>	L.Talley	C.Keeling C.Goyet	J.Bullister	R.Key
P16N*	13	31DSCGC91_2	<i>Discoverer</i>	3/7– 4/8/1991	52 <sup>d</sup>	40	22	50	19 <sup>c</sup>	J.Bullister	R.Feely R.Byrne	J.Bullister	R.Key
P16A17A*	14	316N138_9	<i>Knorr</i>	10/6– 11/25/1992	127 <sup>d</sup>	118 <sup>o</sup>	113 <sup>m</sup>	76	37 <sup>d</sup>	J.Reid	T.Takahashi	W.Smethie R.Weiss	R.Key
P17C*	15	31WTTUNES_1	<i>T.Washington</i>	5/31– 7/11/1991	123 <sup>d</sup>	30 <sup>p</sup>	30 <sup>p</sup>	79	31 <sup>d</sup>	M.Tsuchiya	C.Goyet	R.Fine	R.Key
P17N*	16	325021_1	<i>T.Thompson</i>	5/15– 6/26/1993	148 <sup>d</sup>	75	80	100	25 <sup>d</sup>	D.Musgrave	C.Goyet	R.Fine	R.Key P.Quay
P17E19S*	17	316N138_10	<i>Knorr</i>	12/4/1992– 1/22/1993	106 <sup>d</sup>	104 <sup>o</sup>	96 <sup>m</sup>	60	29 <sup>q</sup>	J.Swift	T.Takahashi	W.Smethie R.Weiss	R.Key

Table 4. (continued)

Section	No	EXPOCODE	Ship	Dates	Total	TCO <sub>2</sub>	TALK	CFC	<sup>14</sup> C	Chief Scientist	Carbon	CFC	<sup>14</sup> C
					Stations						Principal Investigator		
WOCE													
P18*	18	31DSCGC94_1,2,3	<i>Discoverer</i>	1/26– 4/27/1994	193 <sup>d</sup>	182	178	138	33 <sup>r</sup>	J.Bullister R.Feely G.Johnson B.Taft	R.Feely F.Millero	J.Bullister	P.Quay
P19C*	19	316N138_12	<i>Knorr</i>	2/22– 4/13/1993	189 <sup>d</sup>	185 <sup>o</sup>	173 <sup>m</sup>	107	48 <sup>d</sup>	L.Talley	T.Takahashi	R.Fine	R.Key
P21*	20	31MWESTW_4,5	<i>Moana Wave</i>	3/27– 6/25/94	277 <sup>d</sup>	103	108	257	0	H.Bryden M.McCartney	C.Goyet F.Millero C.Winn	J.Bullister R.Fine	NA
P31*	21	3250031_1	<i>T.Thompson</i>	1/25– 2/19/1994	93 <sup>d</sup>	27	26	65 <sup>d</sup>	0	D.Roemmich	C.Winn J.Downing	M.Warner	NA
S04P*	22	90KDIOFFE6_1	<i>A.Ioffe</i>	2/14– 4/6/1992	113 <sup>s,d</sup>	112 <sup>t</sup>	112 <sup>m</sup>	113 <sup>s,d</sup>	30 <sup>d</sup>	M.Koshlyakov	T.Takahashi	J.Bullister M.Warner	P.Schlosser
SR3S4** <sup>aq</sup>	23	09AR9404_1	<i>A.Australis</i>	12/13/1994– 2/2/1995	106 <sup>s,d</sup>	58	58	79	0 <sup>k</sup>	S.Rintoul	B.Tilbrook	J.Bullister	B.Tilbrook
P01 <sup>ap</sup>	24	49EWMI9905_1	<i>Mirai</i>	5/23– 6/11/1999	76 <sup>u</sup>	42	38	0	0 <sup>e</sup>	T.Ono	T.Ono	NA	Fukasawa
EQPAC* <sup>al</sup> Spring	25	EQ92SPR	<i>M.Baldrige</i>	2/27– 5/15/1992	95 <sup>v</sup>	87	95	0	0	D.Atwood R.Feely R.Wanninkhof	R.Feely R.Wanninkhof F.Millero	NA	NA
A21 <sup>am</sup>	26	06MT11_5	<i>Meteor</i>	1/23– 3/8/1990	78 <sup>w</sup>	77	71	72	18	W.Roether	T.Takahashi	W.Roether	P.Schlosser
EQPAC <sup>al</sup> Fall	27	EQ92FAL	<i>Discoverer</i>	9/7– 12/2/1992	103 <sup>v</sup>	101	100	0	0 <sup>k</sup>	R.Feely P.Murphy R.Wanninkhof	R.Byrne R.Feely F.Millero R.Wanninkhof	NA	R.Toggweiler
P11A	28	09AR9391_2	<i>A.Australis</i>	4/4– 5/9/1993	62 <sup>d</sup>	34	0	0	0 <sup>k</sup>	S.Rintoul	B.Tilbrook	NA	B.Tilbrook
P11S	29	09FA693	<i>Franklin</i>	6/24– 7/17/1993	74 <sup>d</sup>	0	0	0	0	J.Church S.Rintoul	NA	NA	NA
P12 <sup>x</sup>	30	09AR9601_1	<i>A.Australis</i>	8/22– 9/22/1996	67 <sup>d</sup>	63	59	0	0	S.Rintoul	B.Tilbrook	NA	NA
P13C	31	49HH915_1,2	<i>Hakuho Maru</i>	8/13– 10/2/1991	69 <sup>d</sup>	0	0	0 <sup>e</sup>	0	K.Taira	NA	S.Watanabe	NA
P14C	32	316N138_7	<i>Knorr</i>	9/1– 9/15/1992	52 <sup>d</sup>	0	0	51	12 <sup>d</sup>	D.Roemmich	J.Downing	M.Warner	R.Key

Table 4. (continued)

Section	No	EXPOCODE	Ship	Dates	Total	TCO <sub>2</sub>	TALK	CFC	<sup>14</sup> C	Chief Scientist	Carbon	CFC	<sup>14</sup> C
					Stations						Principal Investigator		
P01W	33	90BM9316_1	<i>Nesmeyanov</i>	8/30– 9/21/1993	38 <sup>d</sup>	37	30	0	0 <sup>z</sup>	A.Bychkov F.Whitney	A.Bychkov C.S.Wong	C.S.Wong	C.S.Wong
P24	34	49RY9511_2	<i>Ryofu Maru</i>	11/15– 11/30/1995	26 <sup>d</sup>	0	0	9	2	M.Fujimura	NA	K.Nemoto	M.Aoyama
P2E	35	492SSY9310_1,2	<i>Shoyo</i>	10/14– 11/27/1993	131 <sup>d</sup>	0 <sup>aa</sup>	0 <sup>aa</sup>	0 <sup>aa</sup>	0 <sup>aa</sup>	T.Bando Yoritaka	T.Ono	Y.Watanabe	Y.Watanabe
P08N	36	49K6KY9606_1	<i>Kaiyo Maru</i>	6/20– 7/15/1996	25 <sup>d</sup>	25	0 <sup>aa</sup>	25	0 <sup>aa</sup>	K.Mizuno	T.Amaoka K.Yamada	K.Kawahara	T.Tokieda
S5 <sup>ab</sup>	37	09FA1094	<i>Franklin</i>	11/12– 12/5/1994	68 <sup>ac</sup>	0	0	0	0	M.Tomczak	NA	NA	NA
SR3	38	09AR9101_1	<i>A.Australis</i>	9/25– 10/27/1991	26 <sup>d</sup>	0	0	24 <sup>d</sup>	0	S.Rintoul	NA	J.Bullister	NA
P04	39	32MW893_1,2,3	<i>Moana Wave</i>	2/06– 5/19/1989	216 <sup>d</sup>	0	0	159 <sup>d</sup>	0	J.Toole T.Joyce H.Bryden	NA	J.Bullister R.Fine R.Weiss	NA
P03	40	31TTTPS24_1,2	<i>T.Thompson</i>	3/30– 6/3/1985	216 <sup>d</sup>	0	0 <sup>z</sup>	133 <sup>ad</sup>	0	J.Swift D.Roemmich	R.Feely	R.Weiss	NA
P01	41	31TTTPS47_1	<i>T.Thompson</i>	8/4– 9/7/1985	115 <sup>d</sup>	0 <sup>z</sup>	0 <sup>z</sup>	63 <sup>ad</sup>	0	L.Talley	R.Feely	R.Weiss	NA
<b>JGOFS</b>													
KIWI-6	42	RR_KIWI_6	<i>R.Revelle</i>	10/23– 11/17/1997	21 <sup>ae</sup>	11	11	0	0	T.Cowles	F.Millero	NA	NA
KIWI-7	43	RR_KIWI_7	<i>R.Revelle</i>	12/2/1997– 1/3/1998	19 <sup>ae</sup>	19	19	0	0	R.Barber	F.Millero	NA	NA
NBP96_4	44	NBP-96_4	<i>N.B.Palmer</i>	8/30– 9/24/1996	4 <sup>ae</sup>	0	0	0	0	R.Anderson	T.Takahashi	NA	NA
NBP97_1	45	NBP-97_1	<i>N.B.Palmer</i>	1/13– 11/17/1997	28 <sup>ae</sup>	25	0	0	0	J.Marra	T.Takahashi	NA	NA
NBP97_3	46	NBP-97_3	<i>N.B.Palmer</i>	4/4– 5/12/1997	17 <sup>ae</sup>	16	16	0	0	H.Ducklow	F.Millero	NA	NA



Table 4. (continued)

Section	No	EXPOCODE	Ship	Dates	Total	TCO <sub>2</sub>	TALK	CFC	<sup>14</sup> C	Chief Scientist	Carbon	CFC	<sup>14</sup> C
					Stations						Principal Investigator		
Historical													
P16N	47	31WTMARAI	<i>T. Washington</i>	5/5– 6/3/1984	0	0	0	0	0	R.D'Szoek	NA	NA	NA
GEOSECS	48	Leg 1 Leg 2 Leg 3 Leg 4 Leg 5 Leg 6 Leg 7 Leg 8 Leg 9 Leg 10	<i>Melville</i>	8/25– 6/9/1974	147	75 <sup>ag</sup>	75 <sup>ag</sup>	0	44 <sup>ah</sup>	H.Craig W.Broecker T.Takahashi D.Spencer R.Weiss P.Biscaye J.Edmond H.Craig P.Brewer W.Broecker	A. Bainbridge A. Mantyla R. Williams T. Takahashi R. Weiss	NA	G.Östlund M.Stuiver
TEW <sup>an</sup>	49	TEW_WST2	<i>T. Washington</i>	6/6– 7/5/1987	108 <sup>af</sup>	0	0	0 <sup>aj</sup>	0	S.Hayes	NA	D.Wisegarver	NA
P15S	50	MBCGC90_1,2	<i>M. Baldrige</i>	2/22– 4/16/1990	63 <sup>ak</sup>	49 <sup>ak</sup>	0	0	0	D.Wisegarver	R.Feely R.Wanninkhof	J.Bullister	NA

\*Cruise data used in calculating anthropogenic CO<sub>2</sub>.

<sup>a</sup>Not the official WOCE occupation for this line; See cruise No.16 in this table.

<sup>b</sup>See footnote d; Report for this cruise included with P16N.

<sup>c</sup>See Jones 1994, Key et al. 1996.

<sup>d</sup>Final cruise report available at WHPO web site.

<sup>e</sup>Results not yet public.

<sup>f</sup>See Johnson et al. 2001a.

<sup>g</sup>Calculated via MLR; See Sabine et al. 2002a.

<sup>h</sup>See Sabine et al. 2002a,b.

<sup>i</sup>See Dickson et al. 2000.

<sup>j</sup>Spare gas aliquots collected during 13C analysis currently being analyzed for delta 14C.

<sup>k</sup>Analysis not yet completed.

<sup>l</sup>See Takahashi et al. 1996.

<sup>m</sup>Calculated from measured pCO<sub>2</sub> and TCO<sub>2</sub>.

<sup>n</sup>See Goyet et al. 1996.

<sup>o</sup>See Rubin et al. 1998.

<sup>p</sup>See Goyet et al. 1997.

<sup>q</sup>See Key 1996, 1997.

<sup>r</sup>See Key and Quay 1998.

<sup>s</sup>See Chipman et al. 1997.

<sup>t</sup>Data received from T. Ono.

<sup>v</sup>Data downloaded from AOML web site.

<sup>w</sup>See listing under Atlantic Ocean cruises.

<sup>x</sup>Currently listed as SR03 at WHP with repeat hydrography.

<sup>z</sup>Samples collected, status unknown.

<sup>aa</sup>Results not yet reported to WHP.

<sup>ab</sup>Primary listing with Indian Ocean cruises. Included with this data set to provide closure at the southeastern basin intersection south of Africa.

<sup>ac</sup>Data received from B. Huber and B. Haines, LDEO, now available at WHPO.

<sup>ad</sup>See Warner et al. 1996.

<sup>ae</sup>Data from JGOFS web site.

<sup>af</sup>Data received from L. Talley.

<sup>ag</sup>See Östlund et al. 1987.

<sup>ah</sup>See Östlund and Stuiver, 1980.

<sup>ai</sup>West Pacific with an average station latitude of 13.8S.

<sup>aj</sup>Measurements made, but not in database, see Wisegarver et al. 1993, and footnote ad. The nutrient and oxygen data from this cruise are far below WOCE standards.

<sup>ak</sup>See Lamb and Feely 1995.

<sup>al</sup>This was a JGOFS cruise and should have been listed accordingly.

<sup>am</sup>Primary listing with Atlantic Ocean cruises. Included with this data set to provide closure at the southwestern basin intersection at Drake Passage.

<sup>an</sup>West Pacific with an average station latitude of 13.8ES.

<sup>ao</sup>See Key et al. 1996.

<sup>ap</sup>Not the official WOCE occupation of this line.

<sup>aq</sup>Listed at WHPO as one-time occupation of S03/S04I.

Table 5. Atlantic Ocean cruise summary

Section	No	EXPCODE	Ship	Dates	Total	TCO <sub>2</sub> <sup>a</sup>	TALK	CFC	<sup>14</sup> C	Chief scientist	Carbon	CFC	<sup>14</sup> C
					Stations						Principal investigator		
<b>WOCE</b>													
A01E	1	06MT18_1	<i>Meteor</i>	9/2–9/26/1991	57 <sup>b</sup>	30 <sup>c</sup>	0 <sup>d</sup>	0	13	J.Meincke	L.Mintrop D.Wallace	W.Roether	R.Bayer
A01EW	2	06MT30_3	<i>Meteor</i>	11/15–12/19/1994	61 <sup>b</sup>	0 <sup>s</sup>	0 <sup>s</sup>	51	0 <sup>ax</sup>	J.Meincke	B.Schnider H.Thomas	W.Roether A.Putzka	R.Bayer
A01W	3	18HU95011_1	<i>Hudson</i>	6/7–7/5/1995	61 <sup>b</sup>	51	0 <sup>d</sup>	55	0	J.Lazier	P.Jones	R.Gershey	NA
AR07W*	4	18HU98023_1	<i>Hudson</i>	6/22–7/9/1998	40 <sup>e</sup>	23	23	22	0	P.Jones	P.Jones R.Gershey	P.Johnes R.Gershey	NA
A02*	5	06MT30_2	<i>Meteor</i>	10/12–11/12/1994	52 <sup>b</sup>	0 <sup>s</sup>	0 <sup>s</sup>	44	10	P.Kolterman	L.Mintrop A.Körtzinger	W.Roether	R.Bayer
A02	6	06MT39_3	<i>Meteor</i>	6/11–7/3/1997	65 <sup>b</sup>	34	33	53	0	P.Kolterman	D.Wallace	Unknown	NA
A03	7	90CT40_1	<i>Multanovsky</i>	9/11–11/21/1993	124 <sup>b</sup>	0	0	0	0	V.Tereschenkov	NA	NA	NA
A05* <sup>f</sup>	8	31RBOACES24N_2	<i>Brown</i>	1/24–2/23/1998	130 <sup>g</sup>	126	122	76	0 <sup>ay</sup>	K.Lee A.Bitterman	R.Feely F.Millero	J.Bullister	P.Quay
A05	9	29HE06_1-3	<i>Hesperides</i>	7/14–8/15/1992	111 <sup>b</sup>	33 <sup>h</sup>	33 <sup>h</sup>	65	8 <sup>i</sup>	G.Parrilla	F.Millero A.Rios	W.Smethie	W.Broecker
A06	10	35A3CITHER1_2	<i>L'Atalante</i>	2/13–3/19/1993	84 <sup>b</sup>	0 <sup>j</sup>	0 <sup>d</sup>	52	0	C.Colin	C.Oudot	C.Andrie	NA
A07	11	35A3CITHER1_1	<i>L'Atalante</i>	1/2–2/10/1993	119 <sup>b</sup>	0 <sup>j</sup>	0 <sup>d</sup>	87	0	A.Moliere	C.Oudot	C.Andrie	NA
A08*	12	06MT28_1	<i>Meteor</i>	3/29–5/11/1994	126 <sup>b</sup>	50 <sup>k</sup>	50 <sup>k</sup>	70	0	T.Mueller	D.Wallace	A.Putzka	NA
A09*	13	06MT15_3	<i>Meteor</i>	2/10–3/23/1991	111 <sup>b</sup>	30 <sup>l</sup>	30 <sup>l</sup>	70	4	G.Siedler	C.Goyet D.Wallace	D.Wallace	Unknown
A10*	14	06MT22_5	<i>Meteor</i>	12/27/1992–1/31/1993	112 <sup>b</sup>	55 <sup>m</sup>	25 <sup>m</sup>	76	5	T.Mueller	L.Mintrop D.Wallace	W.Roether	Unknown
A11	15	74DI199_1	<i>Discovery</i>	12/22/1992–2/1/1993	91 <sup>b</sup>	0	0	44	0	P.Saunders	NA	Smythe-Wright	NA
A21/A12* <sup>az</sup>	16	06MT11_5	<i>Meteor</i>	1/23–3/8/1990	78 <sup>b</sup>	77 <sup>n</sup>	77 <sup>n</sup>	66	18	W.Roether	T.Takahashi	W.Roether	P.Schlosser
A12	17	06AQANTX_4	<i>Polarstern</i>	5/21–8/5/1992	98 <sup>b</sup>	53	0	81	0	P.Lemke	M.Hoppema	W.Roether	NA
S4A(A12)	18	06AQANTXIII_4	<i>Polarstern</i>	3/17–5/20/1996	100 <sup>b</sup>	90 <sup>ba</sup>	0	92	0	E.Fahrbach	M.Hoppema	A.Watson	NA
A13*	19	35A3CITHER3_2	<i>L'Atalante</i>	2/22–4/2/1995	135 <sup>b</sup>	49	46	134	0	M.Arhan	L.Bingler A.Gonzales	L.Memery	NA
A14*	20	35A3CITHER3_1	<i>L'Atalante</i>	1/11–2/11/1995	107 <sup>b</sup>	53 <sup>p</sup>	102	102	0	H.Mercier	L.Bingler A.Rios	L.Memery	NA

Table 5. (continued)

Section	No	EXPOCODE	Ship	Dates	Total	TCO <sub>2</sub> <sup>a</sup>	TALK	CFC	<sup>14</sup> C	Chief scientist	Carbon	CFC	<sup>14</sup> C
					Stations						Principal investigator		
<b>WOCE</b>													
A15*	21	316N142_3	<i>Knorr</i>	4/3– 5/21/1994	148 <sup>b</sup>	93	93	81	0	W.Smethie G.Weatherly	C.Goyet	W.Smethie	NA
A16S <sup>bb</sup>	22	OACES91_1-2	<i>Baldrige</i>	7/11– 9/2/1991	33 <sup>bc</sup>	33	32	0	0	D.Atwood	F.Millero R.Wanninkhof	NA	NA
A16N* <sup>bb</sup>	23	OACES93	<i>Baldrige</i>	7/4– 8/29/1993	81 <sup>bd</sup>	81	79	80	0 <sup>be</sup>	R.Wanninkhof	F.Millero R.Feely	J.Bullister	P.Quay
A17*	24	3230CITHER2_1-2	<i>M.Ewing</i>	1/4– 3/21/1994	234 <sup>b</sup>	145 <sup>aw</sup>	90	226	0	L.Memery	D.Wallace A.Rios	D.Wallace	NA
A20*	25	316N151_3	<i>Knorr</i>	7/17– 8/10/1997	90 <sup>b</sup>	79 <sup>q</sup>	90 <sup>q</sup>	83	13 <sup>r</sup>	R.Pickart	F.Millero C.Sabine D.Wallace	W.Smethie	R.Key
A22*	26	316N151_4	<i>Knorr</i>	8/15– 9/3/1997	77 <sup>b</sup>	51 <sup>q</sup>	59 <sup>q</sup>	75	11 <sup>r</sup>	T.Joyce	F.Millero C.Sabine D.Wallace	W.Smethie	R.Key
A23	27	74JC10_1	<i>J.C.Ross</i>	3/20– 5/6/1995	127 <sup>b</sup>	0 <sup>i</sup>	0	99	0	K.Heywood B.King	J.Robertson	A.Watson	NA
A24*	28	316N151_2	<i>Knorr</i>	5/30– 7/5/1997	153 <sup>b</sup>	143 <sup>q</sup>	144 <sup>q</sup>	131	0	L.Talley	F.Millero D.Wallace	R.Weiss	NA
A25	29	74DI230_1	<i>Discovery</i>	8/7– 9/17/1997	142 <sup>b</sup>	0 <sup>as</sup>	0 <sup>as</sup>	119	0	S.Bacon	M.Rodriguez	Smythe- Wright	NA
AR24	30	316N147_2	<i>Knorr</i>	11/2– 12/3/1996	188 <sup>e</sup>	54 <sup>q</sup>	55 <sup>q</sup>	0	0	M.McCartney	F.Millero D.Wallace C.Winn	NA	NA
SR02	31	06AQANTVIII_2	<i>Polarstern</i>	9/6/– 10/30/1989	86 <sup>b</sup>	0	0	0 <sup>s</sup>	0 <sup>s</sup>	E.Fahrbach	NA	Unknown	Unknown
SR04	32	06AQANTX_7	<i>Polarstern</i>	12/3/1992– 1/22/1993	78 <sup>b</sup>	65 <sup>bi</sup>	0	0	0	E.Fahrbach	M.Hoppema	NA	NA
I6S <sup>t</sup>	33	35MFCIVA_1	<i>M.Dufresne</i>	1/23– 3/9/1993	52 <sup>b</sup>	52	52	52	8 <sup>v</sup>	A.Poisson	A.Poisson	A.Poisson	M.Arnold
I6Sb* <sup>t</sup>	34	35MF103_1	<i>M.Dufresne</i>	2/20– 3/22/1996	55 <sup>b</sup>	55	55	54	0	A.Poisson	A.Poisson	A.Poisson	NA
<b>Historical</b>													
A12/A13 <sup>bf</sup>	35	316N83_a,c	<i>Knorr</i>	10/7/1983– 2/19/1984	137 <sup>w</sup>	105 <sup>x</sup>	103 <sup>x</sup>	132 <sup>y</sup>	0	J.Reid W.Nowlin	T.Takahashi	R.Weiss	NA
ANT V-2,3	36	06AQANTV_2,3	<i>Polarstern</i>	6/27– 12/14/1986	164 <sup>z</sup>	58 <sup>z</sup>	58 <sup>z</sup>	29 <sup>z</sup>	20 <sup>z</sup>	E.Augstein G.Hempel A.Gordon	T.Takahashi	R.Weiss	P.Schlosser
ARC	37	316N83_b	<i>Knorr</i>	11/13– 12/10/1983	84 <sup>aa</sup>	0	0	0	0	A. Gordon	NA	NA	NA

Table 5. (continued)

Section	No	EXPOCODE	Ship	Dates	Total	TCO <sub>2</sub> <sup>a</sup>	TALK	CFC	<sup>14</sup> C	Chief scientist	Carbon	CFC	<sup>14</sup> C
											Stations		
<b>Historical</b>													
A3	38	3IAN109_1	<i>Atlantis II</i>	6/12– 7/18/1981	101 <sup>ab,au</sup>	0	0	0	0	C Wunsch	NA	NA	NA
Marathon7	39	31WT847	<i>T.Washington</i>	10/1– 10/22/1984	64 <sup>ac</sup>	0	0	63 <sup>bh</sup>	0	A.Gordon	NA	W.Smethie	NA
A20	40	32OC133	<i>Oceanus</i>	5/1– 5/17/1983	94 <sup>ab</sup>	0	0	0	0	M.McCartney	NA	NA	NA
A16N <sup>ad</sup>	41	32OC202_1-2	<i>Oceanus</i>	7/23– 8/27/1988	129 <sup>b</sup>	0	0	78	0	M. McCartney	NA	J.Bullister	NA
WEPOLEX <sup>av</sup>	42	WEPOLEX	<i>M.Somov</i>	10/9– 11/25/1982	24 <sup>ae</sup>	0	24 <sup>ae</sup>	0	0	A. Gordon E. Sarukhanyan	C.Chen	NA	NA
GEOSECS	43	GEOSECS_1-9	<i>Knorr</i>	7/18/1972– 4/1/1973	114 <sup>af</sup>	58 <sup>af</sup>	58 <sup>af</sup>	0	41 <sup>ag</sup>	D.Spencer D.Spencer W.Broecker H.Craig W.Broecker K.Park H.Craig J.Reid T.Takahashi	PACODF	NA	G.Östlund M.Stuiver
A16N	44	06MT56_5	<i>Meteor</i>	3/28– 4/23/1981	29	0	0	0	10 <sup>ah,bg</sup>	W.Roether	NA	NA	W.Roether
TTO-NAS	45	TTONAS_1-7	<i>Knorr</i>	4/1– 10/19/1981	247 <sup>ai</sup>	164 <sup>aj</sup>	164 <sup>aj</sup>	0	62 <sup>ak</sup>	P.Brewer J.Sarmiento L.Armi W.Broecker T.Takahashi W.Jenkins P.Brewer	P.Brewer T.Takahashi	NA	G.Östlund
TTO-TAS	46	TTOTAS_1-3	<i>Knorr</i>	12/1/1982– 2/18/1983	110 <sup>al</sup>	102 <sup>aj</sup>	102 <sup>aj</sup>	0 <sup>am</sup>	39 <sup>ak</sup>	J.Sarmiento C.Rooth T.Takahashi	T.Takahashi	R.Weiss	G.Östlund
WBEX	47	316NXXX	<i>Knorr</i>	4/24– 5/18/1986	51 <sup>an</sup>	0	0	51 <sup>ao</sup>	0	W.Jenkins	NA	W.Smethie	NA
SAVE	48	318MSAVE_1-5 318MHYDROS4 <sup>at</sup>	<i>Knorr</i> (1–3) <i>Melville</i> (4–6)	11/23/1987– 3/8/1989 3/13– 4/19/1989	370 <sup>ap</sup>	360 <sup>ap</sup>	299 <sup>ap</sup>	348	77 <sup>aq</sup>	T.Takahashi W.Smethie W.Jenkins R.Key W.Smethie M.McCartney	T.Takahashi	R.Weiss W.Smethie	G.Östlund

\*Cruise data used in calculating anthropogenic CO<sub>2</sub>.<sup>a</sup>Calibration details for carbon measurements are in Wanninkhof et al. 2003.

<sup>b</sup>Cruise report available at WHPO web site. These cruise reports include the final data reports written specifically for CFCs, carbon measurements and both large volume and small volume radiocarbon measurements.

<sup>c</sup>See Johnson et al. 1996.

<sup>d</sup>Alkalinity measurements from this cruise deleted from merged data set.

<sup>e</sup>Not listed by WHP as a WOCE cruise.

<sup>f</sup>See Peltola et al. 1998.

<sup>g</sup>See Millero et al. 2000.

<sup>h</sup>See Severinghaus et al. 1996.

<sup>i</sup>TCO<sub>2</sub> measurements from this cruise deleted from merged data set .

<sup>k</sup>See Johnson et al. 2002b.

<sup>l</sup>See Johnson et al. 1995.

<sup>m</sup>See Johnson et al. 1998b.

<sup>n</sup>See Chipman et al. 1994.

<sup>p</sup>See Rios et al. 2003 for independent estimates of anthropogenic CO<sub>2</sub> for this section.

<sup>q</sup>See Johnson et al. 2003.

<sup>r</sup>See Elder 2002.

<sup>s</sup>WHP records indicate samples collected, but not yet reported.

<sup>t</sup>Indian Ocean cruise additionally listed here to provide data closure at the southeastern boundary.

<sup>v</sup>See Lebourcier et al. 1999.

<sup>w</sup>See ODF 1985.

<sup>x</sup>See Chipman et al. 1986.

<sup>y</sup>See Weiss et al. 1990.

<sup>z</sup>Hydrographic data received from Bruce Huber, LDEO; nutrient data received from L. Gordon, Oregon State Univ.; carbon data received from Taro Takahashi, LDEO; calculated alkalinity values are from R. Wanninkhof, NOAA/AOML; P.Schlosser isotope data and R.Weiss CFC data received from B.Kromer

<sup>aa</sup>ARC (Agulhas Retroflexion Cruise; data received from B.Huber and B.Haines, LDEO.

<sup>ab</sup>Data received from L.Talley, SIO, see also Woods Hole data Report WHOI 85-38.

<sup>ac</sup>Data received from B.Huber and B.Haines, LDEO.

<sup>ad</sup>Listed by WHP as official occupation of the A16N line.

<sup>ae</sup>See Chen 1987, Gordon et al. 1984, and Gordon and Huber 1984.

<sup>af</sup>See Bainbridge 1981.

<sup>ag</sup>See Östlund et al. 1987.

<sup>ah</sup>Data received from B.Kromer.

<sup>ai</sup>See ODF 1986a.

<sup>aj</sup>See Brewer et al. 1986.

<sup>ak</sup>See Östlund and Grall 1987.

<sup>al</sup>See ODF 1986b.

<sup>am</sup>Data not yet obtained; see Weiss et al. 1991.

<sup>an</sup>See Key et al. 1990; this report only includes results from large volume casts, but rosette samples are also in the data file.

<sup>ao</sup>Data received from W. Smethie.

<sup>ap</sup>See ODF 1992 a,b,c.

<sup>aq</sup>See Östlund and Grall 1992.

<sup>as</sup>No data available, see Alvarez et al. 2003.

<sup>at</sup>Hydros 4 was officially an independent cruise, however it is frequently merged with the SAVE cruises, as is done here.

<sup>au</sup>Roemmich and Wunsch 1985.

<sup>av</sup>U.S-U.S.S.R Weddell Polynya Expedition.

<sup>aw</sup>According to the comparison between TALK measured on A17 and recent cruises (CITHER-3, FICARAM-2, and FICARAM-3), the PIs recommend a correction of -8 µmol/kg for all TALK measurements (Rios et al. 2005, NDP-084).

<sup>ax</sup>Data now available from WHPO.

<sup>ay</sup>NOSAMS data report #04-002, values now available from [http://www.aoml.noaa.gov/ocd/oaces/bottle\\_data.html](http://www.aoml.noaa.gov/ocd/oaces/bottle_data.html).

<sup>az</sup>This cruise frequently included as part of SAVE collection.

<sup>ba</sup>Data received from M.Hoppema via B.Huss. Submitted to WHPO 08/12/05.

<sup>bb</sup>Data from [http://www.aoml.noaa.gov/ocd/oaces/bottle\\_data.html](http://www.aoml.noaa.gov/ocd/oaces/bottle_data.html).

<sup>bc</sup>See Forde et al. 1994.

<sup>bd</sup>See Castle et al. 1998.

<sup>be</sup>Measurements completed 12/04, data will soon be available vis [http://www.aoml.noaa.gov/ocd/oaces/bottle\\_data.html](http://www.aoml.noaa.gov/ocd/oaces/bottle_data.html).

<sup>bf</sup>Commonly known as AJAX Expedition.

<sup>bg</sup>See Schlitzer et al. 1985.

<sup>bh</sup>See Smethie 1993.

<sup>bi</sup>See Hoppema et al. 1995, 1997, 1998; Robinson and Williams 1991.

**Table 6. Summary statistics for data set Gv1.1**

Ocean		WOCE	Hist.	WOCE TCO <sub>2</sub>	Hist. TCO <sub>2</sub>	WOCE TALK	Hist. TALK	WOCE Δ <sup>14</sup> C	Hist. Δ <sup>14</sup> C	WOCE CFC	Hist. CFC	WOCE PALK	Hist. Palk	WOCE AnthCO <sub>2</sub>	Hist. Anth CO <sub>2</sub>	WOCE Bomb <sup>14</sup> C	Hist. Bomb <sup>14</sup> C
<b>Indian</b>																	
	Samples	60961	7573	29261	4005	25480	3781	4705	868	29669	1885	24307	3476	17864	1566	4173	718
	Stations	2167	260	1514	143	1432	144	222	73	1626	117	1403	126	1095	84	222	71
	Cruises	21	3	15	2	14	2	11	2	18	2	14	2	13	1	11	2
<b>Pacific</b>																	
	Samples	131157	13758	42089	3258	36568	2416	10745	872	44098	0	34053	2410	21957	0	8702	741
	Stations	4406	415	2305	124	2091	75	628	44	2509	0	1997	75	1496	0	620	43
	Cruises	45	4	35	2	31	1	21	1	29	0	30	1	25	0	21	1
<b>Atlantic</b>																	
	Samples	79425	55385	32375	16558	24112	13611	1705	2953	46867	13425	21578	13208	19761	0	1505	2147
	Stations	3380	1705	1605	847	1267	808	139	249	2240	701	1224	781	1085	0	122	218
	Cruises	34	14	25	6	20	7	10	6	28	6	20	6	17	0	10	6
<b>Global<sup>a</sup></b>																	
	Samples	258993	76716	95877	23821	80698	19808	15217	4693	112785	15310	74802	19094	55134	1566	12807	3606
	Stations	9497	2380	5092	1114	4554	1027	785	366	6026	818	4396	982	3474	84	766	332
	Cruises	94	21	70	10	61	10	37	9	70	8	60	9	51	1	37	9

<sup>a</sup>The global numbers do not equal the sum of the ocean numbers because cruises near the ocean-to-ocean boundaries were included in both oceans

**Table 7. Parameters and units in GLODAP bottle files**

Col. No.	Parameter <sup>a</sup>	Units
1	Station number <sup>b</sup>	integer
2	Cruise Number <sup>c</sup>	integer
3	Longitude	degrees with west < 0 and east > 0
4	Latitude	degrees with south < 0 and north > 0
5	Month	integer (1–12)
6	Day	integer (1–31)
7	Year	integer (1972–1999)
8	Bottom depth <sup>d</sup>	meters
9	Bottle number <sup>e</sup>	integer
10	Cast <sup>f</sup>	integer
11	Sample depth	meters
12	Temperature	°C
13	Salinity	practical salinity scale -78
14	Oxygen	micromole kilogram <sup>-1</sup>
15	Nitrate	micromole kilogram <sup>-1</sup>
16	Nitrite	micromole kilogram <sup>-1</sup>
17	Silicate	micromole kilogram <sup>-1</sup>
18	Phosphate	micromole kilogram <sup>-1</sup>
19	CFC-11	picomole kilogram <sup>-1</sup>
20	CFC-12	picomole kilogram <sup>-1</sup>
21	Dissolved inorganic carbon	micromole kilogram <sup>-1</sup>
22	Total alkalinity	micromole kilogram <sup>-1</sup>
23	Anthropogenic CO <sub>2</sub>	micromole kilogram <sup>-1</sup>
24	Δ <sup>14</sup> C	‰ (parts per thousand)
25	δ <sup>13</sup> C	‰
26	Δ <sup>14</sup> C counting error	‰
27	Apparent oxygen utilization (AOU)	micromole kilogram <sup>-1</sup>
28	CFC-11 partial pressure	picoatmosphere
29	CFC-11 Age	years
30	CFC-12 partial pressure	picoatmosphere
31	CFC-12 Age	years

<sup>a</sup>Missing values are represented in the data by the value of -9, except for radio carbon, which is -999.

<sup>b</sup>Original station number plus (cruise number -1)\*1000.

<sup>c</sup>Sequential order of cruise in each ocean data set.

<sup>d</sup>Approximate value taken from either the shipboard depth recorder, the maximum CTD lowering pressure + 10, or a global topography.

<sup>e</sup>Generally the listed bottle number, but occasionally the listed sample number. When information was not available, this value was fabricated.

<sup>f</sup>When not included in original data, a value of 1 was generally used. In a few instances where it was obvious that multiple casts had occurred at a station, but no cast numbers were given, the cast value was fabricated.



**Table 8. Indian Ocean correction factors**

Section	No	EXPOCODE	Station Range	Salt <sup>a</sup>	Oxygen	NO <sub>3</sub>	PO <sub>4</sub>	SiO <sub>2</sub>	TCO <sub>2</sub>	TALK
<b>WOCE<sup>b</sup></b>										
16S_b	1	35MF103_1	all	-0.5	-0.025	0	0	0	0	0
IR04(I8R)	2	3175MB95_07								
SR3S4 <sup>c</sup>	3	AR9404_1								
S04a <sup>d</sup>	4	06AQANTXIII_4								
S05	5	09FA1094								
I8A(S04)	6	74DI200_1	all	-0.1	0.206	0.36	0.032	3.8		
ISS01_i	7	74DI213_1	all	0.5 <sup>e</sup>	-0.003	-0.96	0	-8.2		
ISS01_h	8	74DI207	all	0	0	0	0	0		
ISS03_b	9	09FA9605	all	0	0	0	0	0		
IR06_b	10	09FA9508_1	all	0	0	0	0	0		
<b>WOCE<sup>f</sup></b>										
S04I	11	320696_3	all	0	0.001	1.000	1.000	1.000	0	0
I06S	12	35MFCIVA_1	all	0	-0.021	1.000	1.000	1.000	0	0
I08SI09S	13	316N145_5	all	1.4	-0.013	0.9923	0.9904	0.9948	0	0
I09N	14	316N145_6	all	0.4	0.024	0.9961	0.9901	0.9874	0	0
I08NI05E	15	316N145_7	all	1.4	0.016	0.9961	0.9892	0.9981	0	0
I03	16	316N145_8	all	1.3	0.027	1.0048	0.9978	0.9889	0	0
I05WI04	17	316N145_9	all	0.5	-0.002	1.0042	0.9951	0.9933	0	0
I07N	18	316N145_10	all	-0.5	0	0.9827	1.0144	1.0020	0	0

**Table 8. (continued)**

Section	No	EXPOCODE	Station Range	Salt <sup>a</sup>	Oxygen	NO <sub>3</sub>	PO <sub>4</sub>	SiO <sub>2</sub>	TCO <sub>2</sub>	TALK
<b>WOCE<sup>f</sup></b>										
I01	19	316N145_11,12	857-961 962-1014	-0.3 -0.2	0.024 0.014	0.9712 0.9969	1.0374 0.9912	0.9934 0.9913	0 0	0 0
I10	20	316N145_13	all	1.3	0.065	1.0007	0.9963	0.9819	0	0
I02	21	316N145_14	1077-1156 1157-1244	0.7 1.6	0.027 0.027	1.0038 1.0053	1.0058 1.0102	0.9945 1.0015	0 0	0 0
<b>Historical<sup>g</sup></b>										
I05	22	74AB29	all	0.2	0.056	-0.08	0.010	-2.7	0	0
INDIGO-1 INDIGO-2 INDIGO-3	23	INDIGO-1 INDIGO-2 INDIGO-3	1-25 27-69 75-117	-0.07 -1.0 -0.04	0 0.018 0	0 0 0	0 0 0	0 0 0	-10.7 -9.4 -6.4	-6.5 6.8 0
GEOSECS	24	GEOSECS Indian 3-7	402-404 405-426 427-435 436-446 447-454	0 1.4 0 0 0	0 0.030 0 0 0	0 0 0 0 0	0 0 0 0 0	0 0 0 0 0	-22.5 -22.5 -22.5 -22.5 -22.5	0 0 0 0 0

<sup>a</sup>Salinity corrections are in parts per million; i.e., divide factor by 1000 prior to addition.

<sup>b</sup>All factors are additive. Taken from Gouretski and Jancke 2001.

<sup>c</sup>See listings with Pacific Ocean cruises.

<sup>d</sup>See listings with Atlantic Ocean cruises.

<sup>e</sup>L. Gordon and C. Mordy (personal communication, 2003) derived a salt correction of -5.5 for this cruise.

<sup>f</sup>Salinity factors are from Johnson et al. (2003) and are additive. Oxygen factors are from Gouretski and Jancke (2001) and are additive. Their oxygen factors were/are listed in ml/L and were multiplied by 43.55 to convert to  $\mu\text{mol/kg}$  prior to application. Nitrate, phosphate, and silicate factors are from L. Gordon and C. Mordy (2003, personal communication) and are multiplicative. TCO<sub>2</sub> and TALK corrections are from Sabine et al. (1999) and are additive.

<sup>g</sup>Salinity, oxygen, nitrate, phosphate, and silicate factors are from Gouretski and Jancke (2001) and are additive. Their oxygen factors were/are listed in ml/L and were multiplied by 43.55 to convert to  $\mu\text{mol/kg}$  prior to application. Carbon factors are from Sabine et al. (1999) and are additive.

**Table 9. Pacific Ocean correction factors**

Section	No	EXPOCODE	Station Range	Salinity <sup>a</sup>	Oxygen	NO <sub>3</sub>	PO <sub>4</sub>	SiO <sub>2</sub>	TCO <sub>2</sub>	TALK
<b>WOCE<sup>b</sup></b>										
P17N	1	31DSCGC91_1	all	-0.72	1.0147	1.000	0.9870	1.000	-7.0	-12.0
P02	2	50K6KY9401_1	all	0	1.000	1.0200	0.9620	1.000	-4.0	14.0
P06	3	316N138/3,4,5	1-72 75-188 190-267	0.50 -0.59 -1.17	1.0003 1.0036 0.9999	1.000 1.000 1.000	0.9875 0.9914 1.0000	1.000 1.000 1.000	-0.6 -0.6 -0.6	0 0 0
P08S	4	49XK9605	all	1.82	1.0059	1.0159	1.0335	1.0300	2.0	6.0
P09	5	49RY9407_1	1-53 54-105	-0.50 0.77	0.9923 0.9945	0.9900 0.9900	1.000 1.000	1.000 1.000	1.1 1.1	0 0
P10	6	3250TN026/1	all	-0.5	1.0052	1.0150	1.0074	1.0077	0	0
P13N	7	31VIC92_0,1,2	1-55 56-88	0.77 -0.94	1.0131 1.0035	0.9925 1.0450	1.000 1.000	1.000 0.9860	0 0	0 0
P14N	8	325023_1 325024_1	1-130 131-185	1.37 1.12	1.0087 1.0058	1.0014 1.0076	1.0125 1.0125	0.9894 1.000	0 0	0 0
P14S15S	9	31DSCGC96_1,2	1-93 94-182	-0.40 -1.00	1.0041 1.0072	1.000 1.000	1.000 1.000	1.000 1.000	0 0	0 0
P15N	10	18DD9403_1,2	1-70 71-136	1.91 -0.37	1.0068 0.9948	1.0071 1.0000	1.000 0.9874	1.0200 1.0000	0 0	0 0
P16S17S	11	31WTTUNES-2	all	1.80	1.0008	1.0112	1.000	0.9852	1.4	0
P16C	12	31WTTUNES_3	all	-0.47	0.9998	1.000	1.000	0.9935	0	0
P16N	13	31DSCGC91_2	all	-1.21	1.0105	1.000	1.000	0.9877	4.0	0
P16A17A	14	316N138_9	all	-0.39	1.0027	1.000	1.000	0.9926	1.3	0
P17C	15	31WTTUNES_1	all	2.10	1.0017	1.0200	1.0034	1.000	0	-9.0
P17N	16	325021_1	all	-0.72	1.0147	1.000	0.9870	1.000	-7.0	-12.0

Table 9. (continued)

Section	No	EXPOCODE	Station Range	Salinity <sup>a</sup>	Oxygen	NO <sub>3</sub>	PO <sub>4</sub>	SiO <sub>2</sub>	TCO <sub>2</sub>	TALK
WOCE <sup>b</sup>										
P17E19S	17	316N138_10	all	-0.61	1.0100	1.000	0.9923	0.9940	1.4	0
P18	18	31DSCGC94_1,2,3	1-87 88-194	0.37 1.46	1.0114 1.0119	1.000 1.000	1.000 1.000	1.006 1.000	0 0	0 0
P19C	19	316N138/12	all	-0.39	1.0101	0.9920	0.9891	0.9918	-0.2	0
P21	20	31MWESTW_4,5	1-161 162-294	-0.63 -0.210	1.0136 0.9703	1.000 1.0074	0.9888 0.9950	1.000 1.000	0 0	0 0
P31	21	3250031_1	all	0.19	1.0059	1.0164	0.9950	1.000	0	-6.0
S04P	22	90KDIOFFE6_1	all	1.72	1.0013	1.0156	0.9900	0.9809	-0.9	0
SR3S4	23	09AR9404_1	all	-3.50	1.0143	1.000	1.000	1.000	0	0
P01	24	49EWMI9905/1								
EQPAC Spring	25	EQ92SPR								
A21	26	06MT11_5		see Atlantic Ocean table						
EQPAC Fall	27	EQ92FAL								
P11A	28	09AR9309_1,2	all	-6.46	1.0181	1.000	1.000	1.0436	0	0
P11S	29	09FA693	all	2.08	0.9688	0.9270	0.9717	0.9950	0	0
P12	30	09AR9601_1								
P13C	31	49HH915_1,2	1-30 31-68	-2.01 0.27	0.9730 0.9624	1.000 1.000	1.000 1.000	1.000 1.000	0 0	0 0
P14C	32	316N138_7	all	-1.16	0.9989	1.000	1.000	0.9830	0	0
P01W	33	90BM9316_1								

**Table 9. (continued)**

Section	No	EXPOCODE	Station Range	Salinity <sup>a</sup>	Oxygen	NO <sub>3</sub>	PO <sub>4</sub>	SiO <sub>2</sub>	TCO <sub>2</sub>	TALK
P24	34	49RY9511_2	all	-0.56	0.9986	1.000	1.000	1.000	0	0
P2E	35	492SSY9310_1,2	35-96 97-165	1.09 1.83	0.9961 0.9932			1.000 1.000	0 0	0 0
P08N	36	49K6KY9606_1								
S5	37	09FA1094								
SR3	38	09AR9101_1								
P04	39	32MW893_1,2,3	1-83 84-119 120-221	1.57 1.35 -0.92	1.0067 0.9840 0.9899	1.000 1.000 1.000	1.000 1.000 0.9835	1.000 1.000 0.9969	0 0 0	0 0 0
P03	40	31TTTPS24_1,2	1-197 199-408	3.34 3.05	0.9985 0.9971	0.9890 0.9890	1.0220 1.0220	1.000 1.000	0 0	0 0
P01	41	31TTTPS47_1	all	3.26	0.9993	1.000	1.0070	1.000	0	0
<b>JGOFS<sup>c</sup></b>										
KIWI-6	42	RR_KIWI_6								
KIWI-7	43	RR_KIWI_7								
NBP96_4	44	NBP-96_4								
NBP97_1	45	NBP-97_1								
NBP97_3	46	NBP-97_3								
<b>Historical/Other<sup>d</sup></b>										
P16N	47	31WTMARAI	all	-0.021	-0.21	0.85	0.23	5.5		

**Table 9. (continued)**

Section	No	EXPOCODE	Station Range	Salinity <sup>a</sup>	Oxygen	NO <sub>3</sub>	PO <sub>4</sub>	SiO <sub>2</sub>	TCO <sub>2</sub>	TALK
GEOSECS	48	GEOSECS_1-10	201–210	-3.6	0	0	0	0		
			211–218	-3.6	0	0	0	0		
			219–224	-3.6	0	0	0	0		
			225–234	-1.9	-0.042	0.98	-0.050	1.5		
			235–254	-1.9	-0.042	0.98	-0.050	1.5		
			255–278	-1.9	-0.042	0.98	-0.050	1.5		
			279–294	0.1	-0.045	0.41	-0.034	0.9		
			295–314	-1.7	0	0	0	0		
			315–324	0	0	0	0	0		
			325–347	0	0	0	0	0		
			TEW	49	TEW_WST2	all	2.9	-0.114	0	0
P15S	50	MBCGC90_1,2	all	2.4	0	0	0	0		

<sup>a</sup>Salinity corrections are in parts per million, i.e., divided factor by 1000 prior to addition.

<sup>b</sup>Salinity, DIC, and TALK factors are additive. Oxygen, nitrate, phosphate, and silicate factors are multiplicative. Salinity and oxygen factors are from Johnson et al. (2001). Nitrate, phosphate, and silicate factors are from L. Gordon and C. Mordy (2003, personal communication). DIC and TALK corrections are from Lamb et al. (2002).

<sup>c</sup>JGOFS cruises were not included in any of the calibration studies. Therefore, no corrections have been applied.

<sup>d</sup>All factors are additive. Taken from Gouretski and Jancke 2001. Their oxygen factors were/are listed in ml/l and were multiplied by 43.55 to convert to  $\mu\text{mol/kg}$  prior to application.

**Table 10. Atlantic Ocean correction factors**

Section	No	EXPOCODE	Station Range	Salinity <sup>a</sup>	Oxygen	NO <sub>3</sub>	PO <sub>4</sub>	SiO <sub>2</sub>	TCO <sub>2</sub> <sup>b</sup>	TALK
<b>WOCE<sup>c</sup></b>										
A01E	1	06MT18_1	all	-1.7	0.029	0.21	0.054	1.4	0	NA
A01EW	2	06MT30_3	all	-1.5	0.004	0.79	0.061	-0.7	0	0
A01W	3	18HU95011_1	all	0	0	0	0	0	0	NA
AR07	4	18HU98023_1	all	0	0	0	0	0	0	0
A02	5	06MT30_2	all	0.6	0.071	-0.07	0.04	-1.8	0	0
A02	6	06MT39_3	all	-2.5	0.023	0.89	0.015	1.5	0	0
A03	7	90CT40_1	all	-0.1	0.15	-0.1	-0.021	3.5	0	0
A05	8	31RBOACES24N_2	all						0	0
A05	9	29HE06_1-3	all	0.3	-0.007	0.34	0.03	1.9	0	0
A06	10	35A3CITHER1_2	all	2.1	0.01	-0.84	-0.072	0.6	NA	NA
A07	11	35A3CITHER1_1	all	2.4	0.045	-0.31	-0.056	1	NA	NA
A08	12	06MT28_1	all	1.7	-0.156	-1.01	0	-4.2	0	0
A09	13	06MT15_3	all	0.6	-0.154	-0.7	-0.085	-3.2	0	-7.0
A10	14	06MT22_5	all	0.4	0.182	0.92	0.056	1.5	0	0
A11	15	74DI199_1	all	0.6	-0.063	0.12	-0.115	-4.9	0	0
A21/A12	16	06MT11_5	all	1.1	0.03	0.04	-0.006	4.9	0	0
A12	17	06AQANTX_4	all	-1.5	-0.047	-0.02	-0.019	1.0	0	0
S4A(A12)	18	06AQANTXIII_4	all	0.9	-0.144	-0.03	0.025	-3.2	0	0
A13	19	35A3CITHER3_2	all	2.8	0.003	-1.3	-0.153	-3.0	0	0
A14	20	35A3CITHER3_21	all	2.3	0.016	-0.19	-0.033	-1.9	0	0

Table 10. (continued)

Section	No	EXPOCODE	Station Range	Salinity <sup>a</sup>	Oxygen	NO3	PO <sub>4</sub>	SiO <sub>2</sub>	TCO <sub>2</sub> <sup>b</sup>	TALK
<b>WOCE<sup>c</sup></b>										
A15	21	316N142_3	all	0.3	-0.001	-0.3	-0.023	-1.5	0	0
A16S	22	OACES91_1-2	all						0	0
A16N	23	OACES93	1-31 32-83	1.5 2.8	0 <sup>d</sup> -0.116 <sup>d</sup>	0 0	-0.038 -0.032	-2.6 0.4	0 0	0 0
A17	24	3230CITHER2_1-2	all	1.8	0.001	0.06	-0.024	1.6	0	0
A20	25	316N151_3	all	-0.7	-0.006	0.08	0.042	0.8	0	0
A22	26	316N151_4	all	-0.1	-0.041	0.37	0.058	0	0	0
A23	27	74JC10_1	all	1.8	-0.117	-0.8	-0.096	-2.4	NA	0
A24	28	316N151_2	all	-2.4	0.011	0.29	0.037	-0.6	0	0
A25	29	74DI230_1	all	-2.0	0.156	0.58	0.115	1.0	0	0
AR24	30	316N147_2	all	0	0	0	0	0	0	0
SR02a	31	06AQANTVIII_2	all	0	-0.065	-0.4	0	-6.8	0	0
SR04	32	06AQANTX_7	all	0	0	0	0	0	0	0
I6S	33	35MFCIVA_1	all	0	-0.021	1.000	1.000	1.000	0	0
I6Sb	34	35MF103_1	all	-0.5	-0.025	0	0	0	0	0
<b>Historical<sup>e</sup></b>										
A12/A13	35	316N83_a,c	all							
ANT V-2,3	36	06AQANTV-2,3	all							
ARC	37	316N83_b	all	0.6	0	0	0	0		
A3	38	31AN109_1	all	2.0	0.024	0	0.055	2.0		



Table 10. (continued)

Section	No	EXPOCODE	Station Range	Salinity <sup>a</sup>	Oxygen	NO3	PO <sub>4</sub>	SiO <sub>2</sub>	TCO <sub>2</sub> <sup>b</sup>	TALK
Marathon7	39	31WT847	all							
<b>Historical<sup>c</sup></b>										
A20	40	32OC133	all	3.2	0.013	0	0	0		
A16Nad	41	32OC202_1-2	all	-1.8	0.039	-0.17	-0.069	-0.3		
WEPOLEX	42									
GEOSECS	43	GEOSECS_1-9	1-35	0	0	0	0	0		
			36-49	0.5	0	0	0	0		
			50-61	0	0	0	0	0		
			62-75	-4.9	0.015	0	0	0		
			76-94	0	0	0	0	0		
			100-113	-0.7	0	0	0	0		
A16N	44	06MT56_5	all	6.2	0.037	0	0	3.8		
TTO-NAS	45	TTONAS_1-7	1-14	2.0	0.076	1.1	0.089	1.5		
			15-41	-0.1	0.02	0.62	0.089	1.7		
			42-109	0	0.091	0	0	0		
			110-140	0.2	0.056	0.93	0.045	1.9		
			141-171	0	0	0	0	0		
			172-219	0	0	0	0	0		
			220-250	1.1	0.034	0.75	0.059	1.4		
TTO-TAS	46	TTOTAS_1-3	1-54	0	0.031	0.21	0.029	2.3		
			55-94	0.8	0.031	0.68	0.077	3.1		
			95-132	1.2	0.05	0	0	5.7		
WBEX	47	316NXXX	all	4.2	0.73	0.77	0.061	0.6		
SAVE	48	318MSAVE_1-5 318MHYDROS4	1-43	0.8	-0.157	-0.66	-0.059	-0.5		
			44-1.5	0.9	0.023	-0.21	-0.026	-1.6		
			106-170	0.4	0.032	-0.39	-0.027	-1.8		
			171-235	-1.7	0.02	-0.31	-0.001	-0.3		
			236-308	-0.3	0.016	-0.09	-0.039	0.4		
			309-379	-0.5	0.019	-0.28	-0.029	0.3		

<sup>a</sup>Salinity corrections are in parts per million, i.e., divided factor by 1000 prior to addition.

<sup>b</sup>A factor “NA” indicates that the measurements were not retained in the database, generally because of unusual scatter or excessive calibration offset determined by Wanninkhof et al. 2003

<sup>c</sup>Salinity, oxygen, nitrate, phosphate, and silicate factors are from Gouretski and Jancke (2001) and are additive. Their oxygen factors were/are listed in ml/l and were multiplied by 43.55 to convert to  $\mu\text{mol/kg}$  prior to application. Carbon factors are from Wanninkhof et al. 2003 and are additive

<sup>d</sup>Castle et al. 1998 suggested that the oxygen values for this cruise were low by  $7.5 \mu\text{mol/kg}$  ( $\sim 0.17 \text{ ml/l}$ ). Gouretski and Jancke (2001) suggested an oxygen correction of  $5.05 \mu\text{mol/kg}$  for stations 32–83. We inadvertently applied both corrections to these data. The oxygen values for this cruise should be reduced by  $7.5 \mu\text{mol/kg}$  to back out Castle et al. 1998, then the correction for this cruise will be consistent with other oxygen adjustments.

<sup>e</sup>Salinity, oxygen, nitrate, phosphate, and silicate factors are from Gouretski and Jancke (2001) and are additive. Their oxygen factors were/are listed in ml/l and were multiplied by 43.55 to convert to  $\mu\text{mol/kg}$  prior to application

**Table 11. Summary of the TCO<sub>2</sub> quality assessment results**

Cruise	TCO <sub>2</sub> analysis technique	TCO <sub>2</sub> P.I.	Standardization technique	Sample vol. (mL)	CRM correction SIO-cruise	Field replicate analyses average difference	SIO shorebase replicate analyses		
							Average difference shore-ship (μmol/kg)	Std. dev. of difference (μmol/kg)	N
P8S	Coulorimeter	Shitashima	Liquid Standards	30	2.0±2.8	1.8	ND	ND	ND
P9	Coulorimeter	Ishii	Liquid Standards	23	1.1±1.3	2.0	ND	ND	ND
P10	Coulorimeter/ SOMMA	Sabine	Gas Loops	22	±1.9	1.7	0.6	1.8	9
P13	Coulorimeter/ SOMMA	Dickson	Gas Loops <sup>a</sup>	30	±2.4	0.9	1.4	3.1	138
P14N	Coulorimeter/ SOMMA	Winn/ Millero	Gas Loops	20	ND	ND	0.7	2.3	27
P14S15S	Coulorimeter/ SOMMA	Feely	Gas Loops	26	1.1±0.9	1.9	ND	ND	ND
P15N	Coulorimeter/ SOMMA	Wong	Liquid Standards	29	1.1±2.7	ND	ND	ND	ND
EQS92	Coulorimeter/ SOMMA	Feely	Gas Loops	26	1.8±1.2	ND	ND	ND	ND
P16C	Coulorimeter/ SOMMA	Goyet	Liquid Standards <sup>a</sup>	30	ND	ND	2.1	2.4	66
P16N	Coulorimeter	Feely	Liquid Standards	50	3.0±2.5	2.8	ND	ND	ND
P16S17S	Coulorimeter	Takahashi	Gas Loops	20	1.3±1.5	0.03%	3.5	2.0	11
P16A17A	Coulorimeter	Takahashi	Gas Loops	20	1.0±1.7	0.03%	3.4	1.8	14
P17C	Coulorimeter/ SOMMA	Goyet	Liquid Standards <sup>a</sup>	30	0 <sup>b</sup>	ND	3.4	4.0	40
P17N	Coulorimeter/ SOMMA	Goyet	Liquid Standards	30	0 <sup>b</sup>	ND	1.0	4.1	9
CGC91	Coulorimeter	Feely	Liquid Standards	50	3.0±2.5	2.8	ND	ND	ND
P17E19S	Coulorimeter	Takahashi	Gas Loops	20	1.4±2.1	0.03%	ND	ND	ND
P18	Coulorimeter/ SOMMA	Feely	Gas Loops	26	1.3±1.4	2.0	1.4	2.0	28
P19C	Coulorimeter	Takahashi	Gas Loops	20	1.2±2.1	0.03%	1.0	1.9	15
P2	Coulorimeter	Ono	Gas Loops	32	6.8±3.1	ND	ND	ND	ND
P21	Coulorimeter/ SOMMA	Millero	Gas Loops	20	0.9±1.1	ND	2.3	1.5	15
P31	Coulorimeter/ SOMMA	Winn	Gas Loops	21	1.9±2.7	2.0	0.2	3.4	8

**Table 11. (continued)**

Cruise	TCO <sub>2</sub> analysis technique	TCO <sub>2</sub> P.I.	Standardization technique	Sample vol. (mL)	CRM correction SIO-cruise	Field replicate analyses average difference	SIO shorebase replicate analyses		
							Average difference shore-ship (μmol/kg)	Std. dev. of difference (μmol/kg)	N
P6	Coulorimeter/SOMMA	Wallace	Gas Loops	28	10.6±1.9	ND	12.6	1.9	21
S4P	Coulorimeter	Takahashi	Gas Loops	20	10.9±1.8	0.03%	ND	ND	ND
SR3S4	Coulorimeter/SOMMA	Tilbrook	Gas Loops	22	10.0±0.95	2.0	ND	ND	ND

Abbreviations: ND — no data; SOMMA — single-operator multiparameter analyzer.

<sup>a</sup> CRM used as a primary standard.

<sup>b</sup> CRMs were not available.

**Table 12. Summary of TCO<sub>2</sub> crossover results in the Pacific Ocean**

Crossing no.	Latitude	Longitude	Section 1	Section 1 station	Section 2	Section 2 station	ΔTCO <sub>2</sub> st. dev. (μmol/kg)
6	30E N	135E E	P9	21	P2	19, 21	1.6±2.4
10	30E N	148E E	P10	74, 77	P2	37	12.8±1.0
18	63E S	140E E	SR3S4	33	SR3S4	65	10.9±0.5
20	66E S	164E E	SR3S4	51	S4P	791	1.4±2.9
23	30E N	165E E	P13	54, 55	P2	48	15.5±2.1
28	30E N	178E E	P14N	63	P2	58	0.5±2.7
33	31E N	177E E	P6C	188	P6E	191	11.2±0.6
34	66E S	171E E	P14S15S	32	S4P	783, 787	0.4±0.2
36	30E N	165E W	P15N	52, 54	P2	65	15.7±4.0
40a	0E	170E W	P14S15S	174	EQS92	56	2.8±2.3
40b	0E	170E W	P14S15S	174	P15N	112	1.2±0.7
40c	0E	170E W	P15N	112	EQS92	56	1.5±2.0
40d	1E S	170E W	P14S15S	173	P15N	114	3.5±2.9
40e	2E S	170E W	P14S15S	172	P15N	116	10.6±2.0
40f	3E S	170E W	P14S15S	171	P15N	118	4.8±4.0
40h	4E S	170E W	P14S15S	170	P15N	120	3.5±0.9
40i	5E S	170E W	P14S15S	169	EQS92	63	12.6±1.2

**Table 12. (continued)**

Crossing no.	Latitude	Longitude	Section 1	Section 1 station	Section 2	Section 2 station	$\Delta\text{TCO}_2$ st. dev. ( $\mu\text{mol/kg}$ )
40j	5E S	170E W	P14S15S	169	P15N	122	6.3±1.3
40k	5E S	170E W	P15N	122	EQS92	63	!8.6±2.3
40l	6E S	170E W	P14S15S	167	P15N	124	0.0±0.8
40m	7E S	170E W	P14S15S	165	P15N	126	2.8±0.7
40n	8E S	170E W	P14S15S	163	P15N	128	2.5±2.3
40o	12E S	170E W	P14S15S	155	P15N	134, 136	1.4±1.1
41a	10E S	170E W	P14S15S	157, 159, 161	P15N	130, 132	0.9±0.7
41b	10E S	170E W	P14S15S	157, 159, 161	EQS92	66	!1.5±3.0
41c	10E S	170E W	P14S15S	157, 159, 161	P31	54, 57, 61	!2.6±2.2
41d	10E S	170E W	P15N	130, 132	EQS92	66	!2.4±2.2
41e	10E S	170E W	EQS92	66	P31	54, 57, 61	!0.8±5.8
41f	10E S	170E W	P15N	130, 132	P31	54, 57, 61	!3.2±3.6
42	17E S	170E W	P14S15S	141, 142, 144	P21	193, 195, 197	!2.3±0.4
43	32E S	170E W	P14S15S	110, 112, 114	P6	153, 165	!1.4±2.1
44	40E S	173E W	P14S15S/1	93	P14S15S/2	94	1.5±4.7
45	67E S	169E W	P14S15S	33	S4P	755	5.2±0.9
47	53E N	152E W	P16N	58, 59, 66	P17N	78	!9.0±5.1
49	30E N	152E W	P16N	30, 31, 32	P2	70	!7.6±3.0
53a	17E S	150E W	P16C	222	P16S17S	220	!1.1±1.5
53b	17E S	150E W	P16C	222	P31	2, 5	0.6±0.8
53c	17E S	150E W	P16C	222	P21	157, 160	!1.4±1.4
53d	17E S	150E W	P16S17S	220	P31	2, 5	0.9±0.5
53e	17E S	150E W	P16S17S	220	P21	157, 160	!0.8±1.0
53f	17E S	150E W	P21	157, 160	P31	2, 5	2.7±3.3
54	32E S	150E W	P16S17S	190	P6	127, 129	5.9±4.7
55	37E S	150E W	P16S17S	180	P16A17A	3	0.1±2.4
59	40E N	135E W	CGC91/1	10	P17N	37, 38, 45	!7.9±1.5

**Table 12. (continued)**

Crossing no.	Latitude	Longitude	Section 1	Section 1 station	Section 2	Section 2 station	$\Delta\text{TCO}_2$ st. dev. ( $\mu\text{mol/kg}$ )
60a	35E N	135E W	CGC91/1	12	P17N	28	!3.7 $\pm$ 5.1
60b	35E N	135E W	CGC91/1	12	P17C	17	5.7 $\pm$ 3.7
60c	35E N	135E W	P17N	28	P17C	17	9.4 $\pm$ 3.4
61	30E N	135E W	P17C	26	P2	78	!3.1 $\pm$ 4.6
64	6E S	135E W	P17C	121	P16S17S	124	!1.0 $\pm$ 2.5
65	16E S	133E W	P16S17S	148	P21	131	!0.5 $\pm$ 1.7
66a	33E S	135E W	P16S17S	179	P6	108	0.8 $\pm$ 1.0
66b	33E S	135E W	P16S17S	179	P16A17A	119	2.8 $\pm$ 2.2
66c	33E S	135E W	P16A17A	119	P6	108	!2.3 $\pm$ 0.7
67	53E S	135E W	P16A17A	77	P17E19S	128	!4.4 $\pm$ 2.9
68	66E S	126E W	P17E19S	163	S4P	723, 727	!1.1 $\pm$ 1.5
73	5E N	110E W	P18	155, 159	EQS92	6	!7.5 $\pm$ 4.9
74	17E S	103E W	P18	105, 106	P21	77	!2.7 $\pm$ 1.5
76	32E S	103E W	P18	73	P6	56, 58	!0.5 $\pm$ 0.4
77	52E S	103E W	P18	37	P17E19S	194	3.4 $\pm$ 0.8
78	67E S	103E W	P18	10, 11	S4P	711, 712, 713	!1.2 $\pm$ 0.4
80	16E S	86E W	P19	333	P21	49	!3.1 $\pm$ 0.9
81	32E S	88E W	P19	299	P6	32, 34, 36	!0.5 $\pm$ 0.1
82	53E S	88E W	P19	256	P17E19S	206	1.8 $\pm$ 0.9
83	67E S	88E W	S4P	703	P17E19S	229	!0.9 $\pm$ 1.5
<b>Average: !0.3<math>\pm</math>3.9</b>							

**Table 13. Summary of the TALK quality assessment results**

Cruise name	TALK analysis technique	P.I. name	Sample volume (mL)	Shore-based st. dev. ( $\mu\text{mol/kg}$ )	No. of shore-based observations
P8S	Potentiometric	Shitashima	50	4.3	17
P9	ND	ND	ND	ND	ND
P10	Potentiometric	Sabine	100	ND	ND
P13	Potentiometric	Guenther/Keeling	91	ND	ND

**Table 13. (continued)**

Cruise name	TALK analysis technique	P.I. name	Sample volume (mL)	Shore-based st. dev. ( $\mu\text{mol/kg}$ )	No. of shore-based observations
P14N	Potentiometric	Millero	200	ND	ND
P14S15S	Potentiometric	Millero	200	ND	ND
P15N	Potentiometric	Wong	203	ND	ND
EQS92	Potentiometric	Millero	200	ND	ND
P15C	Potentiometric	Guenther/Keeling	91	ND	ND
P16N	ND	ND	ND	ND	ND
P16S17S	Potentiometric	Goyet	100	3.2	12
P16A17A	ND	ND	ND	ND	ND
P17C	Potentiometric	Goyet	100	9.0	24
P17N	Potentiometric <sup>a</sup>	Goyet	100	ND	ND
CGC91	ND	ND	ND	ND	ND
P17E19S	ND	ND	ND	ND	ND
P18	Potentiometric	Millero	200	ND	ND
P19C	ND	ND	ND	ND	ND
P2	Potentiometric	Ono	150	ND	ND
P21	Potentiometric	Millero	200	ND	ND
P31	Potentiometric	Winn	200	ND	ND
P6	ND	ND	ND	ND	ND
S4P	ND	ND	ND	ND	ND
SR3S4	Potentiometric	Tilbrook	210	ND	ND

ND — No data

<sup>a</sup> CRMs not analyzed.

**Table 14. Summary of TALK crossover results in the Pacific Ocean**

Crossing no.	Latitude	Longitude	Section 1	Section 1 station	Section 2	Section 2 station	$\Delta\text{TALK st. dev.}$ ( $\mu\text{mol/kg}$ )
10	30E N	148E E	P10	74, 77	P2	37	16.9 $\pm$ 9.7
18	63E S	140E E	SR3S4	33	SR3S4	65	4.1 $\pm$ 2.2
20	66E S	164E E	SR3S4	51	S4P	791	1.2 $\pm$ 1.1
23	30E N	165E E	P13	54, 55	P2	48	12.9 $\pm$ 1.2

Table 14. (continued)

Crossing no.	Latitude	Longitude	Section 1	Section 1 station	Section 2	Section 2 station	$\Delta$ TALK st. dev. ( $\mu\text{mol/kg}$ )
28	30E N	178E E	P14N	63	P2	58	8.4 $\pm$ 2.4
34	66E S	171E E	P14S15S	32	S4P	783, 787	5.6 $\pm$ 1.6
36	30E N	165E W	P15N	52, 54	P2	65	14.8 $\pm$ 6.7
40a	0E	170E W	P14S15S	174	EQS92	56	11.7 $\pm$ 3.9
40b	0E	170E W	P14S15S	174	P15N	112	11.0 $\pm$ 3.2
40c	0E	170E W	P15N	112	EQS92	56	114.6 $\pm$ 4.9
40d	1E S	170E W	P14S15S	173	P15N	114	6.3 $\pm$ 2.4
40e	2E S	170E W	P14S15S	172	P15N	116	4.8 $\pm$ 3.5
40f	3E S	170E W	P14S15S	171	P15N	118	4.5 $\pm$ 5.6
40h	4E S	170E W	P14S15S	170	P15N	120	1.0 $\pm$ 3.2
40i	5E S	170E W	P14S15S	169	EQS92	63	5.9 $\pm$ 2.0
40j	5E S	170E W	P14S15S	169	P15N	122	4.1 $\pm$ 2.7
40k	5E S	170E W	P15N	122	EQS92	63	6.6 $\pm$ 1.9
40l	6E S	170E W	P14S15S	167	P15N	124	2.6 $\pm$ 4.6
40m	7E S	170E W	P14S15S	165	P15N	126	1.9 $\pm$ 1.4
40n	8E S	170E W	P14S15S	163	P15N	128	2.2 $\pm$ 0.6
40o	12E S	170E W	P14S15S	155	P15N	134, 136	2.8 $\pm$ 1.0
41a	10E S	170E W	P14S15S	157, 159, 161	P15N	130, 132	2.4 $\pm$ 1.8
41b	10E S	170E W	P14S15S	157, 159, 161	EQS92	66	0.2 $\pm$ 3.8
41c	10E S	170E W	P14S15S	157, 159, 161	P31	54, 57, 61	10.5 $\pm$ 3.5
41d	10E S	170E W	P15N	130, 132	EQS92	66	10.7 $\pm$ 2.7
41e	10E S	170E W	EQS92	66	P31	54, 57, 61	17.3 $\pm$ 2.3
41f	10E S	170E W	P15N	130, 132	P31	54, 57, 61	13.2 $\pm$ 0.9
42	17E S	170E W	P14S15S	141, 142, 144	P21	193, 195, 197	0.34 $\pm$ 0.35
44	40E S	173E W	P14S15S/1	93	P14S15S/2	94	10.4 $\pm$ 5.0
45	67E S	169E W	P14S15S	33	S4P	755	7.0 $\pm$ 1.0
47	53E N	152E W	P16N	58, 59, 66	P17N	78	123.6 $\pm$ 5.8



Table 14. (continued)

Crossing no.	Latitude	Longitude	Section 1	Section 1 station	Section 2	Section 2 station	$\Delta$ TALK st. dev. ( $\mu\text{mol/kg}$ )
49	30E N	152E W	P16N	30, 31, 32	P2	70	3.2 $\pm$ 0.2
53a	17E S	150E W	P16C	222	P16S17S	220	10.6 $\pm$ 3.3
53b	17E S	150E W	P16C	222	P31	2, 5	13.5 $\pm$ 0.9
53c	17E S	150E W	P16C	222	P21	157, 160	10.4 $\pm$ 2.2
53d	17E S	150E W	P16S17S	220	P31	2, 5	16.5 $\pm$ 1.1
53e	17E S	150E W	P16S17S	220	P21	157, 160	7.1 $\pm$ 0.9
53f	17E S	150E W	P21	157, 160	P31	2, 5	15.8 $\pm$ 3.5
64	6E S	135E W	P17C	121	P16S17S	124	0.8 $\pm$ 1.5
65	16E S	133E W	P16S17S	148	P21	131	120.5 $\pm$ 1.7
73	5E N	110E W	P18	155, 159	EQS92	6	10.4 $\pm$ 1.0
74	17E S	103E W	P18	105, 106	P21	77	10.5 $\pm$ 2.8
77	52E S	103E W	P18	37	P17E19S	194	4.5 $\pm$ 1.8
78	67E S	103E W	P18	10, 11	S4P	711, 712, 713	1.0 $\pm$ 1.3
80	16E S	86E W	P19	333	P21	49	12.9 $\pm$ 1.6
<b>Average: 1.1<math>\pm</math>7.6</b>							

Table 15. Summary of totals for selected calculated parameters in Gv1.1 database

Ocean		WOCE PALK	Hist. Palk	WOCE Anth CO <sub>2</sub>	Hist. Anth CO <sub>2</sub>	WOCE Bomb <sup>14</sup> C	Hist. Bomb <sup>14</sup> C
<b>Indian</b>							
	Samples	24307	3476	17864	1566	4173	718
	Stations	1403	126	1095	84	222	71
	Cruises	14	2	13	1	11	2
<b>Pacific</b>							
	Samples	34053	2410	21957	0	8702	741
	Stations	1997	75	1496	0	620	43
	Cruises	30	1	25	0	21	1
<b>Atlantic</b>							
	Samples	21578	13208	19761	0	1505	2147
	Stations	1224	781	1085	0	122	218
	Cruises	20	6	17	0	10	6



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**APPENDIX A:**

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## **APPENDIX B:**

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**APPENDIX F:**

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