NOAA DATA REPORT ERL PMEL-61a

CHEMICAL AND HYDROGRAPHIC MEASUREMENTS IN THE EASTERN PACIFIC DURING THE CGC94 EXPEDITION (WOCE SECTION P18)

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March 1997

Contribution No. 1755 from NOAA/Pacific Marine Environmental Laboratory

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NOTE: Due to an error in the data tables, this is a revised version of the NOAA Data Report ERL PMEL-61 titled "Chemical and Hydrographic Measurements in the Eastern Pacific During the CGC94 Expedition (WOCE Section P18)."

This new version has been given a different report number: NOAA Data Report ERL PMEL-61a.

Please disregard NOAA Data Report ERL PMEL-61.

Contribution No. 1755 from NOAA/Pacific Marine Environmental Laboratory

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REMOTE ACCESS TO DATA LISTED IN THIS REPORT

The data presented in this report is available on a computerized Remote Bulletin Board System (RBIS), Internet FTP, and the World Wide Web (WWW). For information regarding electronic access to the data sets contact:

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Contoured sections of the data are also available at http://www.pmel.noaa.gov/CO2/

The evaluation of the CGC94 dissolved oxygen, nutrients, and CFC measurements by the WOCE Data Quality Experts and WOCE Hydrographic Office has not been completed. After completion of this process, revised versions of these data will be available from the WOCE Hydrographic Office, or by contacting bullister@pmel.noaa.gov.

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Chemical and Hydrographic Measurements in the Eastern Pacific During the CGC94 Expedition (WOCE Section P18)

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ABSTRACT. NOAA's Climate and Global Change (CGC) Program sponsored a major cooperative effort in the eastern Pacific along WOCE Hydrographic Programme Line P18 from 26 January to 27 April 1994. The first leg (Leg 1) consisted of a transit from Seattle to Punta Arenas, Chile. The second leg (Leg 2) covered hydrographic stations from 67°S, 103°W to 27°S, 103°W. The third leg (Leg 3) included stations between 26.5°S, 103°W and 23°N, 110°W. Full depth CTD/rosette casts were made to the ocean bottom at a nominal spacing of 30 miles on Legs 2 and 3. Water samples were collected on the casts for analyses of concentrations of salinity, DO, CFC, fCO_2, DIC, TAlk, pH, TOC/TON, $^{13}C/^{12}C$ isotopes, and nutrients. Biological parameters were also sampled, and included biogenic Si, chlorophyll-a, phaeopigments, and primary productivity.

1. INTRODUCTION

Human activity is rapidly changing the trace gas composition of the earth's atmosphere, causing the greenhouse warming effect from excess carbon dioxide (CO_2) along with other trace gas species such as chlorofluorocarbons, methane, and nitrous oxide. These gases play a critical role in controlling the earth's climate because they increase the infrared opacity of the atmosphere, causing the planetary surface to warm. Of all the anthropogenic CO_2 that has ever been produced, only about half remains in the atmosphere; the global ocean is considered to be the dominant sink for the "missing" CO_2.

The National Oceanic and Atmospheric Administration's (NOAA) Ocean-Atmosphere Carbon Exchange Study (OACES) Program, and the Ocean Tracers and Hydrography Program, in cooperation with the World Ocean Circulation Experiment (WOCE) and the U.S. Joint Global Ocean Flux Study (U.S. JGOFS), participated in a multifaceted oceanographic research cruise conducted aboard the NOAA ship *Discoverer* from 26 January 1994 to 27 April 1994. This hydrographic section is identified as P18 in the WOCE Implementation Plan. The objective of this effort was to 1) describe water properties and relate them to circulation processes throughout the water column in the eastern Pacific Ocean; 2) determine the souces and sinks of carbon dioxide along a line between 103° and 110°W; 3) study the invasion of the ocean by chlorofluorocarbons;

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and 4) provide a high-quality set of baseline measurements for the continuing evaluation of changes in ocean content of dissolved gasses, water properties, and circulation. Underway Acoustic Doppler Current Profiler (ADCP) measurements were made along the track, and Autonomous Lagrangian Circulation Explorer (ALACE) floats were released at designated positions. In addition, underway measurements of surface pH, fCO_2, nitrate (by wet chemistry), photosynthetically available radiation, and fluorescence were collected on a continuous basis throughout the cruise. This data report summarizes the measurements of chlorofluorocarbons (CFC), dissolved inorganic carbon (DIC), CO_2 fugacity (fCO_2), total alkalinity (TAlk), total organic carbon (TOC), pH, $^{13}C/^{12}C$ isotopes ($\delta^{13}C$), silicate ($Si(OH)_4$), biogenic silica, phosphate (PO_4^{3-}) nitrate (NO_3^-), nitrite (NO_2^-), total organic nitrogen (TON), dissolved oxygen (DO), chlorophyll-*a*, phaeopigments, primary productivity, temperature, and salinity. The tabulated bottle data, beam attenuation due to particles, and CTD temperature and salinity data from the CTD casts are given in Appendix A; bottle data from Kevlar™ casts (biological parameters) are presented in Appendix B. This report does not address the underway measurements or the data from the ALACE floats.

1.1 Cruise Itinerary

The first leg (Leg 1a, 1b) departed Seattle, Washington, on 26 January 1994 and performed two shallow test casts in Puget Sound to check equipment. The ship then steamed to the East Blanco Depression off the Washington/Oregon coast, where significant volcanic activity had been detected. A total of six water column CTD/rosette stations were occupied at this site. The ship then proceeded to San Francisco for a touch-and-go on 30 January 1994; after disembarking several scientists, *Discoverer* left for Punta Arenas, Chile. No hydrographic data from Leg 1 are included in this report. Underway measurements were conducted for pH, pCO_2, nitrous oxide, methyl bromide, salinity, and temperature from the ship's underway sea water system (Lobert *et al*., 1996; Wanninkhof *et al*., in prep.).

The second leg (Leg 2) departed Punta Arenas on 22 February 1994. The ship steamed from the entrance of the Strait of Magellan to the first station at 103°W, 67°S; two test casts were conducted en route. Seventy-eight stations were occupied along 103°W; following WOCE Hydrographic Programme (WHP) protocol, station spacing was 30 nautical miles (nm). Between 58°30′S and 48°S, station spacing was increased to 40 nm due to time constraints. The last station occupied on Leg 2 was at 103°W, 26°S, and the ship inported at Isla de Pascua, Chile (Easter Island) on 24 March.

The third leg (Leg 3) departed Isla de Pascua on 29 March 1994 and proceeded to 103°W, 25°30′S; 30-nm spacing was resumed along 103°W to 10°S. Stations were occupied at 40-nm intervals along a dogleg from 103°W, 10°S to 110°20′W, 5°S, over the East Pacific Rise. Spacing of 30 nm was resumed from 5°S to 3°S along 110°20′W. Station spacing was reduced to 20-nm from 3°S to 3°N to obtain better resolution over the equatorial region. From 3°N to 22°30′N, stations were occupied at 30-nm intervals, except from 12°N to 16°N, where spacing was again increased to 40 nm. A gradual shift in longitude from 110°20′W to 110°W was made between 8°N and 10°N. North of 22°30′N, station spacing was reduced to as little as 3 nm over the rapidly shoaling bathymetry approaching Cabo San Lucas, Mexico. The last station occupied was at 110°W, 22°51′N, in less than 200 m of water, and the cruise ended in San Diego on 27 April 1994. Station locations (CTD) and dates are contained in Fig. 1 and Table 1.

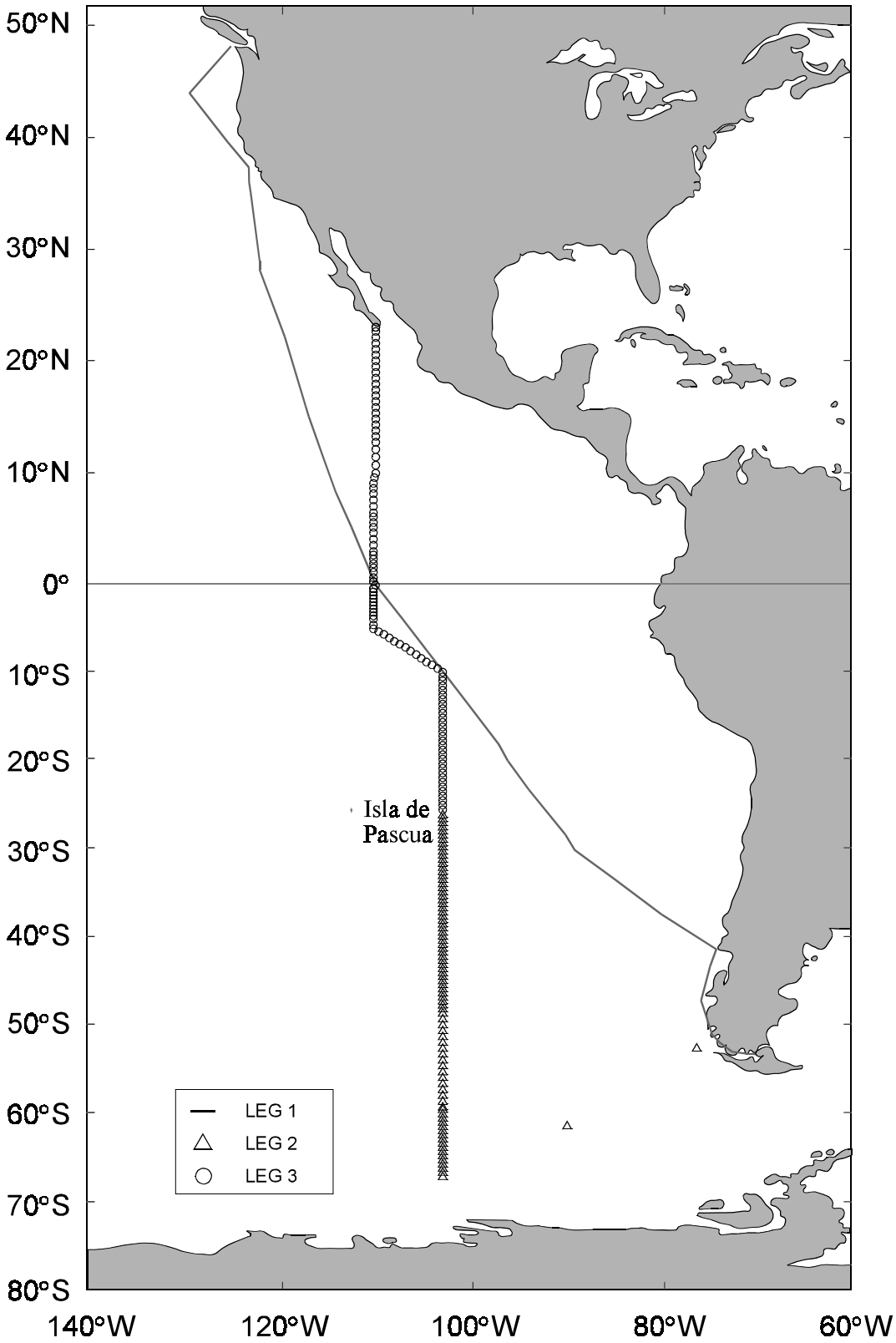

Fig. 1. CTD station locations.

Table 1. CTD station locations and dates during the eastern Pacific 1994 cruise.

Station	Latitude	Longitude	Date	Bottom Depth (m)
Leg 2				
8(test)	52° 22.9′ S	76° 22.0′ W	23 Feb 94	1888
9(test)	61° 13.2′ S	90° 10.9′ W	25 Feb 94	4917
10	66° 59.8′ S	103° 0.2′ W	27 Feb 94	4734
11	66° 29.8′ S	102° 59.9′ W	28 Feb 94	4807
12	66° 0.0′ S	102° 59.8′ W	28 Feb 94	4856
13	65° 29.9′ S	102° 59.9′ W	28 Feb 94	4900
14	64° 59.9′ S	103° 0.0′ W	28 Feb 94	4949
15	64° 29.9′ S	102° 59.9′ W	1 Mar 94	4979
16	63° 59.5′ S	102° 59.1′ W	1 Mar 94	5050
17	63° 30.0′ S	102° 59.6′ W	2 Mar 94	4987
18	63° 0.1′ S	102° 58.4′ W	2 Mar 94	5037
19	62° 29.7′ S	103° 0.5′ W	2 Mar 94	5041
20	61° 59.8′ S	102° 59.8′ W	2 Mar 94	5079
21	61° 29.2′ S	102° 59.3′ W	3 Mar 94	5143
22	61° 0.5′ S	103° 0.3′ W	3 Mar 94	4975
23	60° 30.9′ S	102° 57.1′ W	3 Mar 94	5240
24	60° 0.2′ S	103° 0.0′ W	4 Mar 94	5100
25	59° 30.3′ S	103° 1.6′ W	4 Mar 94	4931
26	59° 0.0′ S	103° 0.9′ W	4 Mar 94	4700
27	58° 30.3′ S	102° 59.7′ W	5 Mar 94	4796
28	57° 49.6′ S	102° 59.4′ W	5 Mar 94	4700
29	57° 10.3′ S	103° 0.1′ W	6 Mar 94	4100
30	56° 31.5′ S	103° 4.9′ W	7 Mar 94	4900
31	55° 50.2′ S	102° 59.9′ W	8 Mar 94	4662
32	55° 9.5′ S	102° 59.5′ W	8 Mar 94	4523
33	54° 30.0′ S	103° 0.0′ W	8 Mar 94	4100
34	53° 49.9′ S	102° 59.0′ W	8 Mar 94	4260
35	53° 10.0′ S	103° 0.9′ W	9 Mar 94	4100
36	52° 30.4′ S	103° 0.4′ W	9 Mar 94	4433
37	51° 50.0′ S	103° 0.0′ W	9 Mar 94	4048
38	51° 10.0′ S	103° 0.0′ W	10 Mar 94	3758
39	50° 30.0′ S	103° 0.5′ W	10 Mar 94	5180
40	49° 50.0′ S	103° 0.1′ W	10 Mar 94	4200
41	49° 9.8′ S	103° 0.3′ W	11 Mar 94	4272
42	48° 29.8′ S	102° 59.7′ W	11 Mar 94	4205
43	47° 59.8′ S	103° 0.4′ W	11 Mar 94	4085
44	47° 30.0′ S	103° 0.1′ W	11 Mar 94	4300
45	47° 0.0′ S	102° 59.8′ W	12 Mar 94	4017
46	46° 30.0′ S	103° 0.0′ W	12 Mar 94	3854
47	46° 0.0′ S	103° 0.0′ W	12 Mar 94	4437
48	45° 28.9′ S	102° 58.4′ W	12 Mar 94	4035
49	45° 0.1′ S	102° 59.9′ W	13 Mar 94	3740
50	44° 29.5′ S	102° 59.7′ W	13 Mar 94	3900
51	43° 59.2′ S	102° 59.8′ W	13 Mar 94	4100
52	43° 30.1′ S	103° 0.9′ W	13 Mar 94	3750

Table 1. (continued)

Station	Latitude	Longitude	Date	Bottom Depth (m)
Leg 2 (continued)				
53	43° 0.2′ S	102° 59.9′ W	14 Mar 94	3790
54	42° 29.5′ S	102° 59.6′ W	14 Mar 94	3791
55	41° 59.7′ S	103° 0.2′ W	14 Mar 94	3672
56	41° 29.6′ S	102° 59.5′ W	15 Mar 94	3780
57	41° 0.0′ S	103° 0.0′ W	15 Mar 94	4803
58	40° 30.2′ S	102° 59.2′ W	15 Mar 94	3930
59	40° 0.2′ S	102° 58.8′ W	15 Mar 94	4058
60	39° 29.9′ S	102° 59.9′ W	16 Mar 94	3917
61	39° 0.0′ S	103° 0.2′ W	16 Mar 94	3834
62	38° 30.6′ S	103° 0.9′ W	16 Mar 94	3990
63	37° 59.9′ S	102° 59.9′ W	16 Mar 94	4143
64	37° 29.9′ S	102° 59.0′ W	17 Mar 94	3498
65	36° 59.7′ S	103° 0.3′ W	17 Mar 94	4050
66	36° 29.9′ S	103° 0.1′ W	17 Mar 94	3479
67	35° 59.6′ S	102° 59.5′ W	17 Mar 94	4483
68	35° 30.0′ S	103° 0.0′ W	18 Mar 94	3099
69	34° 59.9′ S	103° 0.2′ W	18 Mar 94	3600
70	34° 30.8′ S	103° 0.2′ W	18 Mar 94	3434
71	34° 0.4′ S	103° 0.0′ W	18 Mar 94	3730
72	33° 30.0′ S	102° 59.9′ W	19 Mar 94	3592
73	32° 59.7′ S	102° 59.9′ W	19 Mar 94	3682
74	32° 30.0′ S	103° 0.0′ W	19 Mar 94	3569
75	31° 59.7′ S	102° 59.9′ W	19 Mar 94	3830
76	31° 29.5′ S	103° 0.0′ W	20 Mar 94	3532
77	31° 0.1′ S	103° 0.4′ W	20 Mar 94	3489
78	30° 30.1′ S	103° 0.9′ W	20 Mar 94	3410
79	30° 0.0′ S	103° 0.0′ W	21 Mar 94	3586
80	29° 29.5′ S	103° 0.3′ W	21 Mar 94	3400
81	29° 0.1′ S	103° 0.8′ W	21 Mar 94	3546
82	28° 29.7′ S	102° 59.8′ W	22 Mar 94	3287
83	28° 1.0′ S	103° 0.9′ W	22 Mar 94	3347
84	27° 30.7′ S	103° 1.1′ W	22 Mar 94	3059
85	26° 55.2′ S	103° 0.5′ W	22 Mar 94	3139
86	26° 29.7′ S	103° 0.0′ W	23 Mar 94	3463
87	25° 59.4′ S	103° 0.3′ W	23 Mar 94	3454
Leg 3				
88	25° 29.9′ S	103° 0.0′ W	29 Mar 94	3326
89	24° 59.3′ S	103° 0.1′ W	29 Mar 94	3844
90	24° 30.0′ S	103° 0.0′ W	29 Mar 94	3584
91	23° 59.9′ S	103° 0.1′ W	29 Mar 94	3856
92	23° 29.8′ S	102° 59.7′ W	30 Mar 94	3893
93	23° 0.0′ S	102° 59.8′ W	30 Mar 94	3900
94	22° 29.9′ S	103° 0.0′ W	30 Mar 94	4009
95	21° 59.6′ S	102° 59.4 W	30 Mar 94	3953

Table 1. (continued)

Station	Latitude	Longitude	Date	Bottom Depth (m)
Leg 3 (continued)				
96	21° 30.0′ S	102° 59.9′ W	31 Mar 94	3993
97	20° 59.9′ S	103° 0.1′ W	31 Mar 94	4079
98	20° 30.1′ S	103° 0.1′ W	31 Mar 94	4067
99	20° 0.0′ S	103° 0.0′ W	1 Apr 94	4108
100	19° 30.1′ S	102° 59.5′ W	1 Apr 94	4110
101	18° 59.9′ S	103° 0.1′ W	1 Apr 94	4094
102	18° 30.0′ S	103° 0.0′ W	2 Apr 94	4047
103	17° 59.9′ S	103° 0.2′ W	2 Apr 94	4186
104	17° 29.9′ S	103° 0.4′ W	2 Apr 94	4043
105	16° 59.9′ S	102° 59.7′ W	2 Apr 94	3905
106	16° 29.9′ S	103° 0.0′ W	3 Apr 94	3114
107	16° 0.0′ S	103° 0.0′ W	3 Apr 94	3785
108	15° 30.1′ S	103° 0.1′ W	3 Apr 94	3727
109	15° 0.0′ S	102° 59.9′ W	3 Apr 94	4203
110	14° 30.2′ S	102° 59.4′ W	4 Apr 94	3992
111	14° 0.0′ S	102° 59.6′ W	4 Apr 94	4177
112	13° 29.9′ S	103° 0.2′ W	4 Apr 94	4127
113	13° 0.6′ S	103° 0.5′ W	5 Apr 94	4320
114	12° 30.1′ S	103° 0.1′ W	5 Apr 94	4184
115	12° 0.1′ S	103° 0.1′ W	5 Apr 94	4352
116	11° 30.3′ S	103° 0.0′ W	5 Apr 94	4096
117	11° 0.0′ S	103° 0.8′ W	6 Apr 94	4276
118	10° 30.4′ S	103° 0.1′ W	6 Apr 94	4682
119	10° 0.2′ S	103° 0.0′ W	6 Apr 94	4560
120	9° 38.9′ S	103° 36.6′ W	7 Apr 94	4300
121	9° 14.2′ S	104° 8.1′ W	7 Apr 94	4107
122	8° 51.2 S	104° 41.6′ W	7 Apr 94	3713
123	8° 27.8′ S	105° 15.6′ W	7 Apr 94	3655
124	8° 4.7′ S	105° 49.6′ W	8 Apr 94	3993
125	7° 42.0′ S	106° 23.0′ W	8 Apr 94	3245
126	7° 18.7′ S	106° 56.6′ W	8 Apr 94	3181
127	6° 56.4′ S	107° 30.7′ W	9 Apr 94	3179
128	6° 33.6′ S	108° 4.4′ W	9 Apr 94	3286
129	6° 9.3′ S	108° 38.5′ W	9 Apr 94	3300
130	5° 46.4′ S	109° 12.2′ W	9 Apr 94	3474
131	5° 23.6′ S	109° 46.0′ W	10 Apr 94	3800
132	5° 0.1′ S	110° 20.1′ W	10 Apr 94	3448
133	4° 29.7′ S	110° 19.6′ W	10 Apr 94	3810
134	4° 0.2′ S	110° 19.8′ W	10 Apr 94	3873
135	3° 30.0′ S	110° 20.0′ W	11 Apr 94	3915
136	3° 0.0′ S	110° 20.0′ W	11 Apr 94	3914
137	2° 40.0′ S	110° 20.0′ W	11 Apr 94	3900
138	2° 20.0′ S	110° 20.0′ W	11 Apr 94	4616
139	2° 0.8′ S	110° 20.5′ W	12 Apr 94	3978
140	1° 40.0′ S	110° 19.9′ W	12 Apr 94	3907

Table 1. (continued)

Station	Latitude	Longitude	Date	Bottom Depth (m)
Leg 3 (continued)				
141	1° 20.0′ S	110° 20.1′ W	12 Apr 94	3900
142	1° 0.1′ S	110° 19.7′ W	13 Apr 94	4049
143	0° 40.3′ S	110° 19.8′ W	13 Apr 94	3810
144	0° 20.2′ S	110° 19.6′ W	13 Apr 94	3811
145	0° 0.0′ N	110° 0.0′ W	13 Apr 94	3784
146	0° 20.1′ N	110° 20.0′ W	14 Apr 94	3850
147	0° 39.9′ N	110° 20.2′ W	14 Apr 94	3851
148	1° 0.0′ N	110° 20.0′ W	14 Apr 94	3700
149	1° 20.0′ N	110° 20.0′ W	14 Apr 94	3772
150	1° 40.6′ N	110° 20.2′ W	15 Apr 94	3834
151	2° 0.2′ N	110° 20.0′ W	15 Apr 94	3835
152	2° 20.0′ N	110° 20.0′ W	15 Apr 94	3700
153	2° 40.0′ N	110° 19.9′ W	15 Apr 94	3761
154	3° 0.0′ N	110° 20.0′ W	15 Apr 94	3770
155	3° 30.0′ N	110° 20.0′ W	16 Apr 94	3918
156	4° 0.1′ N	110° 20.1′ W	16 Apr 94	3841
157	4° 30.0′ N	110° 20.0′ W	16 Apr 94	3984
158	4° 59.7′ N	110° 20.0′ W	17 Apr 94	4196
159	5° 30.0′ N	110° 20.0′ W	17 Apr 94	3935
160	6° 0.0′ N	110° 20.0′ W	17 Apr 94	3850
161	6° 30.0′ N	110° 20.0′ W	17 Apr 94	3254
162	7° 0.0′ N	110° 20.4′ W	18 Apr 94	3840
163	7° 30.0′ N	110° 20.1′ W	18 Apr 94	3952
164	7° 59.9′ N	110° 20.2′ W	18 Apr 94	3943
165	8° 30.0′ N	110° 15.1′ W	18 Apr 94	3900
166	9° 0.0′ N	110° 9.9′ W	19 Apr 94	3672
167	9° 30.7′ N	110° 5.1′ W	19 Apr 94	3471
168	10° 0.0′ N	110° 0.0′ W	19 Apr 94	3316
169	10° 40.0′ N	110° 0.0′ W	20 Apr 94	3853
170	11° 20.0′ N	110° 0.0′ W	20 Apr 94	3500
171	12° 0.1′ N	110° 0.0′ W	20 Apr 94	3300
172	12° 40.0′ N	110° 0.0′ W	20 Apr 94	4157
173	13° 20.0′ N	109° 59.9′ W	21 Apr 94	4100
174	14° 0.1′ N	109° 59.9′ ′W	21 Apr 94	3284
175	14° 29.8′ N	109° 59.8′ W	21 Apr 94	3724
176	15° 0.0′ N	110° 0.0′ W	21 Apr 94	3792
177	15° 29.8′ N	109° 59.7′ W	22 Apr 94	3739
178	16° 0.1′ N	110° 0.0′ W	22 Apr 94	3307
179	16° 29.9′ N	110° 0.1′ W	22 Apr 94	3397
180	17° 0.0′ N	110° 0.0′ W	22 Apr 94	3520
181	17° 30.1′ N	109° 59.9′ W	23 Apr 94	3485
182	18° 0.0′ N	110° 0.0′ W	23 Apr 94	3265
183	18° 30.0′ N	110° 0.0′ W	23 Apr 94	3440
184	19° 0.0′ N	110° 0.0′ W	23 Apr 94	3372
185	19° 30.0′ N	110° 0.0′ W	24 Apr 94	3238

Table 1. (continued)

Station	Latitude	Longitude	Date	Bottom Depth (m)
Leg 3 (continued)				
186	20° 0.1′ N	110° 0.0′ W	24 Apr 94	2627
187	20° 30.0′ N	110° 0.0′ W	24 Apr 94	3100
188	21° 0.0′ N	110° 0.0′ W	24 Apr 94	3234
189	21° 29 .9′ N	110° 0.1′ W	24 Apr 94	3203
190	21° 59.9′ N	110° 0.0′ W	25 Apr 94	3142
191	22° 29.7′ N	109° 59.7′ W	25 Apr 94	3081
192	22° 44.0′ N	110° 0.4′ W	25 Apr 94	1997
193	22° 47.8′ N	110° 0.3′ W	25 Apr 94	967
194	22° 51.1′ N	110° 0.0′ W	25 Apr 94	190

2. SAMPLING AND ANALYTICAL METHODS

2.1 CTD Cast Operations

CTD/DO measurements were made using one of two Sea Bird 9plus CTDs, each equipped with a fixed pumped temperature–conductivity (TC) sensor pair. A mobile pumped TC pair with dissolved oxygen sensor was mounted on whichever CTD was in use so that dual TC measurements and dissolved oxygen measurements were always collected. The TC pairs were monitored for calibration drift and shifts by examining the differences between the two pairs on each CTD and comparing CTD salinities with bottle salinity measurements.

The primary CTD package utilized PMEL's Sea Bird 9plus CTD (S/N 09P8431-0315) (sampling rate 24 Hz) mounted in a 36-position frame. Water samples were collected using a General Oceanics 36-bottle rosette and 10-liter PVC bottles, and was used for the majority of 194 casts. The secondary package was deployed during foul weather at 29 stations, and used PMEL's Sea Bird 9plus CTD (S/N 329053-0209) (sampling rate 24 Hz) mounted in a 24-position frame, and 4-liter bottles.

The 4- and 10-liter sample bottles mounted on the CTD rosette frames were specially designed Niskin™-type PVC bottles (sometimes referred to as "Bullister" bottles) with internal epoxy-coated stainless steel springs. The O-rings were mounted in a dovetail-shaped groove in the endcaps and sealed against the smooth, flat ends of the bottle. This minimized contact of the seawater sample with the O-rings after closure, and reduced CFC contamination due to O-rings.

All pre- and post-cruise sensor calibrations were performed at Sea-Bird Electronics, Inc. in Bellevue, Washington. Post-cruise data processing was completed at PMEL (McTaggart *et al.*, 1996). Final data are 1-dbar averages in EPIC format (Soreide *et al.*, 1995).

Samples from the CTD casts were collected from the PVC bottles in the following order: chlorofluorocarbons (CFC), helium (He), dissolved oxygen (DO), fugacity of CO_2 (fCO_2), pH, dissolved inorganic carbon (DIC) and total alkalinity (TAlk), tritium, $^{13}C/^{12}C$ isotopes ($\delta^{13}C$), oxygen isotopes, nutrients, total organic carbon (TOC) and nitrogen (TON), chlorophyll-a, phaeopigments, and salinities. This report does not address He, tritium, or oxygen isotope measurements.

2.1.1 Chlorofluorocarbons (CFC)

CFC samples were collected from the PVC bottles before any other samples and were drawn into 100-mL glass syringes. The syringes were sealed with nickel-plated metal stopcocks and positive pressure was maintained with a rubber band. The syringes were stored in a bath of clean seawater until analysis to reduce contamination from the atmosphere.

The bath and the CFC analytical equipment were set up in a seagoing container modified for use as a laboratory. This removed the system from the interior of the ship, which frequently experiences high levels of CFC contamination from air conditioners, water coolers, etc.

The analytical system used for the CFCs was a purge and trap, gas chromatograph/electron capture detector (gc/ECD) system described in Bullister and Weiss (1988). The CFCs were stripped

from an aliquot of the sample with clean carrier gas (95:5 argon:methane), dried over $Mg(ClO_4)_2$, and concentrated on a cold trap of Porasil C™ and Porapak T™. The contents of the trap were injected onto a precolumn of Porasil C™ which vented late unwanted peaks while transferring the gases of interest to a longer Porasil C™ column for final separation. The gases exited the analytical column into an electron capture detector.

About once an hour, a single loop injection of standard was analyzed to monitor changes in sensitivity of the detector. Every few days a number of standard volumes were analyzed to determine changes in sensitivity over a range of responses. The responses of water samples could then be compared to a curve fit through these calibration points. The standard tank used during this cruise (#32386) was calibrated against primary tank #36743 and values assigned on the SIO1986 scale. The concentrations of water samples are reported in picomoles CFC per kilogram (pmol/kg) of seawater.

Sampling blanks may be determined by several methods, including measuring water samples from regions where CFCs have not yet penetrated, and by water bottle incubation tests. Using these methods, the sampling blanks are estimated to have ranged from 0.0048 to 0.0086 pmol/kg for CFC-11, and were 0.0025 pmol/kg or less for CFC-12. During the first 10 stations of Leg 2, the PVC bottles were slightly contaminated with respect to CFC-11. This caused a high variability in the CFC-11/CFC-12 ratio for the deep water samples and, as a result, a larger than normal number of the measurements were flagged as bad or questionable. As the level of contamination in the 10-L bottles declined, the number of flagged samples diminished.

At nearly every station, one or more sets of replicate pairs were drawn and sampled for CFCs. We estimated measurement precision to be about 0.005 pmol/kg or 1% (whichever was greater) for both CFC-11 and CFC-12.

2.1.2 Dissolved Oxygen (DO)

DO samples were drawn from the PVC bottles immediately after CFC and He samples, and were collected in calibrated iodine determination flasks (Corning™ 5400-125) according to the following procedure. The sampling tube was attached to the PVC bottle petcock and the other end inserted into the flask. Seawater was allowed to flow freely into the flask, and the tube was tapped to remove bubbles. The flask was then inverted and the tube pinched slightly to reduce flow while allowing water to drain from the flask. A water sheet formed on the inside of the flask, the sampling tube was pinched off, and the flask was drained and then put right side up. The sampling tube was slowly released to prevent turbulent flow, and the flask was allowed to fill. Fill time was measured to ensure overflow of at least two flask volumes. Typical fill time was 7 seconds.

After a sample was drawn, reagents were introduced quickly using a calibrated Brinkmann™ 1.0-mL Fixed Volume Dispensette repipette with tip lengthened by clear polyolefin shrink tubing. Distilled water or, later, seawater, was added to the collar of the flask to prevent intrusion of air; samples were kept in darkness until analysis. Flasks were reshaken at least 20 minutes after

sampling was finished. All reagents were prepared according to WOCE specifications (WOCE, 1991).

Samples were titrated using Carpenter's whole bottle technique (Carpenter, 1965). An auto-titrator, based on a design by Gernot Friederich (Friederich, 1991) and using a modified version of Friederich's software, was used to titrate the samples. The titrator consists of a Kloehn™ 50100 Syringe Drive with a 5-mL syringe, a custom-built photometer, and a computer. Post-processing software was used to add temperature corrections and to analyze data. The estimated relative accuracy is 0.2%, with an estimated precision of 0.3 µmol/kg.

Samples were analyzed no sooner than 20 minutes and no later than 8 hours after remixing. Liquid from the flask collar was aspirated with a transfer pipette and the stopper removed. Approximately 1 mL of 10N sulfuric acid (H_2SO_4) and a rinsed stir bar were added. The flask was wiped dry, placed in the titrator, and titrated with 0.05 N sodium thiosulfate ($Na_2S_2O_4$). After completion of analysis, the sample was poured out and the flask rinsed with hot tap water.

Titrant was standardized with 0.01N potassium iodate (KIO_3) solution mixed before the cruise and stored in an upside-down airtight bottle. Standard was dispensed using a Kloehn™ 50100 with a calibrated 5-mL buret. The measured precision of the dispensed standards was 0.6 µL and 2.3 µL for volumes below and above 5 mL, respectively. Standards were all within 0.1% of their calculated values when intercompared after the cruise. Concentrations were converted to µmol/kg using sigma-theta. Oxygen values from samples with a sampling or analytical problem are flagged as "3" (questionable) in the data table. Several samples were clearly anomalous relative to surrounding samples in the water column, and to the CTD oxygen sensor. This may have been due to errors in logging the oxygen flask number correctly on the sample log at the time of sample collection, or other labeling errors. These samples are also flagged as questionable.

2.1.3 Discrete Fugacity of CO_2 (fCO_2)

Samples were drawn from the PVC bottles into 500-mL Pyrex™ volumetric flasks using Tygon™ tubing. Bottles were rinsed once and filled from the bottom, overflowing half a volume, and care was taken not to entrain any bubbles. Five mL of water was withdrawn with a pipette to create a small expansion volume. 0.2 mL of saturated $HgCl_2$ solution was added as a preservative. The sample bottles were sealed with a screw cap containing a polyethylene liner and stored upside-down at room temperature for a maximum of a day.

The discrete fCO_2 system is patterned after the setup described in Chipman *et al.* (1993) and is discussed in detail in Wanninkhof and Thoning (1993) and Chen *et al.* (1995). The major difference is that our system uses a LI-COR™ (Model 6262) non-dispersive infrared analyzer, while the system of Chipman *et al.* (1993) utilizes a gas chromatograph with a flame ionization detector and a methanizer which quantitatively converts CO_2 into CH_4 for analysis.

The samples were brought to a temperature of 20.00 ± 0.02°C by inserting the flasks first upside-down in a pre-bath at 19–21°C and subsequently in a Neslab™ (Model RT-220) controlled

temperature bath for equilibration and analysis. A 60-mL headspace was created in the sample flask by displacing the water using a compressed standard gas with a CO_2 mixing ratio close to the fCO_2 of the water.

The headspace contents was circulated in a closed loop through the infrared analyzer, which measured CO_2 and water vapor levels in the sample cell. The headspace contents of two flasks were equilibrated simultaneously in two channels. While the headspace contents of the flask in the first channel flowed through the IR analyzer, that of the flask in the second channel was recirculated in a closed loop. After the first sample was analyzed a valve was switched to put the second channel in line with the analyzer. The samples were equilibrated until the running mean of twenty consecutive 1-second readings from the analyzer had a standard deviation of less than 0.1 ppm (parts per million by volume), which on average took about 10 minutes. An expandable volume consisting of a balloon kept the flask contents at room pressure. In order to maintain measurement precision, a set of six gas standards was run through the system after every eight to twelve seawater samples. The standards had mixing ratios of 201.4, 354.1, 517.0, 804.5, 1012.2, and 2020 ppm, which bracketed most of the fCO_2 at 20°C (fCO_2 (20)) values observed in the water column.

The determination of $fCO_2(20)$ in the headspace contents involved several steps. The IR detector response for the standards was normalized for temperature, the IR analyzer voltage output for samples was normalized to 1 atm pressure, and the IR detector response was corrected for the influence of water vapor. The sample values were converted to a mixing ratio based on the compressed gas standards. The mixing ratio in the headspace contents was converted to fugacity and corrected to the fugacity of CO_2 in the water sample prior to equilibration by accounting for change in total CO_2 in water during the equilibration process (for details see Wanninkhof and Thoning, 1993). The change in $fCO_2(20)$ caused by the change in DIC is calculated using the constraint that TAlk remains constant during exchange of CO_2 gas between the headspace and the water. The calculation is outlined in the appendix of Peng *et al.* (1987).

Relative error of the fCO_2 analysis was determined in two different ways: duplicate samples were taken from PVC bottles tripped at the same depth, and duplicates were taken from the same PVC bottle (Table 2). The difference in relative error between the two types of duplicates was insignificant. The percent relative error is expressed as the absolute difference divided by the mean for two samples.

2.1.4 pH

Seawater samples were drawn from the PVC bottles with a 25-cm length of silicon tubing. One end of the tubing was fit over the petcock of the PVC bottle and the other end was attached over the opening of a 10-cm glass spectrophotometric cell. The spectrophotometric cell was rinsed three to four times with a total volume of approximately 200 mL of seawater; the Teflon™ endcaps were also rinsed and then used to trap a sample of seawater in the glass cell. While drawing the sample, care was taken to make sure that no air bubbles were trapped within the cell.

Table 2. Relative errors for fCO_2 analyses during the eastern Pacific 1994 cruise.

	Samples from different PVC bottles, same depth	Samples from same PVC bottle
Total sets (n)	55	52
Sets used (n)	52	47
Relative error (%)	0.19	0.20

Note: Duplicate samples whose relative error was three times larger than the relative error were omitted from the analyses. The number of sets omitted is the difference between total sets and sets used.

Seawater pH was measured using a double-wavelength spectrophotometric procedure (Byrne, 1987) and the indicator calibration of Clayton and Byrne (1993). The indicator was a 8.0-mM solution of Kodak™ *m*-cresol purple sodium salt ($C_{21}H_{17}O_5Na$) in a 10% ethanol solution; the absorbance ratio of the concentrated indicator solution (RI = 578A/434A) was 1.00. All absorbance ratio measurements were obtained in the thermostatted (25.0 ± 0.05°C) cell compartments of Varian™ CARY 1 and CARY 3 UV-visible dual-beam spectrophotometers. Periodically the spectrophotometric cells were cleaned with a 1 N HCl solution to preclude biological growth.

Measurements of pH were taken at 25.0°C on the total hydrogen ion concentration ($[H^+]_t$) scale, in mol/kg soln:

$$pH_t = -\log[H^+]_t = -\log([H^+]_f\,(1 + [SO_4^{2-}]/K_s)\,)$$

where $[H^+]_f$ represents the concentration of free hydrogen ions in the solution; $[SO_4^{2-}]$ represents the total concentration of sulfate ions in seawater; and K_s represents the dissociation constant of bisulfate ion in seawater.

2.1.5 Dissolved Inorganic Carbon (DIC)

Samples were drawn from the PVC bottles into cleaned, precombusted 500-mL Pyrex™ bottles using Tygon™ tubing according to procedures outlined in the Handbook of Methods for CO_2 Analysis (DOE, 1994). Bottles were rinsed once and filled from the bottom, overflowing half a volume, and care was taken not to entrain any bubbles. The tube was pinched off and withdrawn, creating a 5-mL headspace, and 0.2 mL of saturated $HgCl_2$ solution was added as a preservative. The sample bottles were sealed with glass stoppers lightly covered with Apiezon-L™ grease, and were stored at room temperature for a maximum of 12 hours prior to analysis.

The DIC analytical equipment was set up in a seagoing container modified for use as a laboratory. The analysis was done by coulometry; two analytical systems (PMEL-1 and PMEL-2) were used simultaneously on the cruise, each consisting of a coulometer (UIC, Inc.) coupled with a SOMMA (Single Operator Multiparameter Metabolic Analyzer) inlet system developed by Ken

Johnson (Johnson *et al.*, 1985,1987,1993; Johnson, 1992) of Brookhaven National Laboratory (BNL).

In the coulometric analysis of DIC, all carbonate species (CO_3^{2-} and HCO_3^-) were converted to CO_2 (gas) by addition of excess H^+ to seawater. The analysis was conducted as follows. The 500-mL sample bottle was inserted in a water bath at 20°C and allowed to come to thermal equilibrium; water from the bottle was displaced into a calibrated, thermostatted pipette using a headspace gas (511 ppm CO_2 in N_2). Using Ultra-Pure™ N_2 as the carrier gas, the sample was injected into the reaction vessel in the SOMMA which contained 1 mL 10% H_3PO_4 solution (previously stripped of CO_2), and the evolved CO_2 gas from the sample was carried through a condenser and a $Mg(ClO_4)_2$ column to dry the gas stream, and then through an ORBO-53™ tube to remove volatile acids other than CO_2. In the titration cell of the coulometer, CO_2 reacted quantitatively with ethanolamine to form hydroxyethyl carbamic acid which was titrated with OH^- ions electrogenerated by the reduction of H_2O at a platinum cathode. The equivalence point was detected photometrically with thymolphthalein as indicator. The cell solution was blue at the equivalence point of 10.5 pH and colorless at pH 9.3 after the addition of CO_2 in aqueous solution (Johnson *et al.*, 1985). CO_2 lowers pH and raises % transmittance. As the acid was titrated, pH increased (hence, the blue color returned) and % transmittance decreased, thus causing the titration current to decrease as the equivalence point was approached and sensed by the optical detector. CO_2 was thus measured by the quantity of electrons required to reach the equivalence point, calculated by the magnitude of the current and the passage of time.

The coulometers were calibrated by injecting aliquots of pure CO_2 (99.995%) by means of an 8-port valve outfitted with two sample loops that had been calibrated at BNL (Wilke, 1993). All DIC values were corrected for dilution by 0.2 mL of $HgCl_2$ solution, assuming the solution was saturated with atmospheric CO_2 levels; total water volume was 540 mL. The correction factor used was 1.00037. No correction was made for headspace gas exchange with the sample due to the probable variability of fCO_2 at the location of sampling, and the small magnitude (<1.0 µmol/kg) of the correction.

The instruments were calibrated at the beginning, middle, and end of each coulometer cell solution with a set of the gas loop injections. Using the calculation of CO_2 injected (DOE, 1994), the set of gas loops yielded a mean calibration factor (CF) for the instrument defined as

$$CF = \frac{\text{calculated number of moles } CO_2 \text{ injected from gas loop}}{\text{observed moles of } CO_2 \text{ injected}}$$

The concentration of DIC in the samples was determined according to

$$\text{DIC (µmol/kg)} = \frac{CF \times (\text{Counts} - \text{Blank} \times \text{Run Time}) \times 2.0728 \times 10^{-4}\ \text{µmol/count}}{\text{Pipette Volume} \times \text{Density of Sample}}$$

where “Counts” is the instrument reading at the end of the analysis; “Blank” is the counts/minute determined from blank runs performed at least once for each cell solution; “Run Time” is the length of coulometric titration (in minutes); and 2.0728×10^{-4} is the conversion factor from counts to µmol.

Pipette volume was determined by taking aliquots of distilled water at known temperature dispensed from the pipette before, during, and after the cruise and weighing them ashore. No significant volume change was observed for either instrument. The weights with the appropriate densities were used to determine the volume of the pipette (DOE, 1994).

A Certified Reference Material (CRM) consisting of seawater poisoned with $HgCl_2$ (Batch 19), prepared by Dr. Andrew Dickson (SIO), was analyzed on both instruments over the duration of the cruise (Fig. 2). The CRM value was determined by the manometric technique of Dr. Charles Keeling of SIO. All DIC data have been corrected to the CRM values on a per instrument/per leg basis; the corrections applied are given in Table 3.

The overall uncertainty of the DIC measurements was determined in several different ways. Figure 2 and Table 3 display measurements of the CRMs analyzed during the cruise; no significant trends were observed over time, and the precision was within ±1.9 µmol/kg DIC. From Stations T1 and 192, replicate measurements from different PVC bottles tripped at the same depth, along with replicate measurements from the same PVC bottle, are shown in Table 4. The precision for all samples was within ±1.2 µmol/kg DIC. Duplicate data from the same PVC bottles tripped at 10 m and 1000 m throughout the cruise and analyzed at sea are shown in Table 5. Samples from these pairs were analyzed randomly throughout the life of the coulometer cell solution (25 mg C total throughput), and one remaining sample from one of the pairs was analyzed utilizing a new coulometer cell and solutions. The relative error for these samples was within 0.015%. In addition, sample pairs were collected for shore-based analyses and compared against at-sea analyses. These results are discussed in Section 2.2.5.1.

PMEL has shown a long-term improvement in precision of DIC analyses. Table 6 displays results of CRMs analyzed during cruises in which PMEL has participated from 1990 to 1994. The major improvement in overall precision occurred in 1992 when PMEL scientists began using the SOMMA coulometer system as their primary system for DIC analyses.

2.1.5.1 Shore-based analyses. In addition to the DIC samples analyzed at sea, samples were also collected for post-cruise analyses at SIO’s shore laboratory using a vacuum extraction/manometric analysis method (Guenther, 1994). Pairs of samples for manometric analysis, along with companion samples for at-sea coulometric analysis, were collected at a number of stations throughout the cruise, and were generally drawn from PVC bottles at both 10 and 3000 db (Fig. 3). The data imply a precision of 2.0 µmol/kg for individual shipboard measurements. Using Student’s *t* test (DOE, 1994), the average difference between shore-based and at-sea analyses was not significantly different from zero at the 95% confidence level.

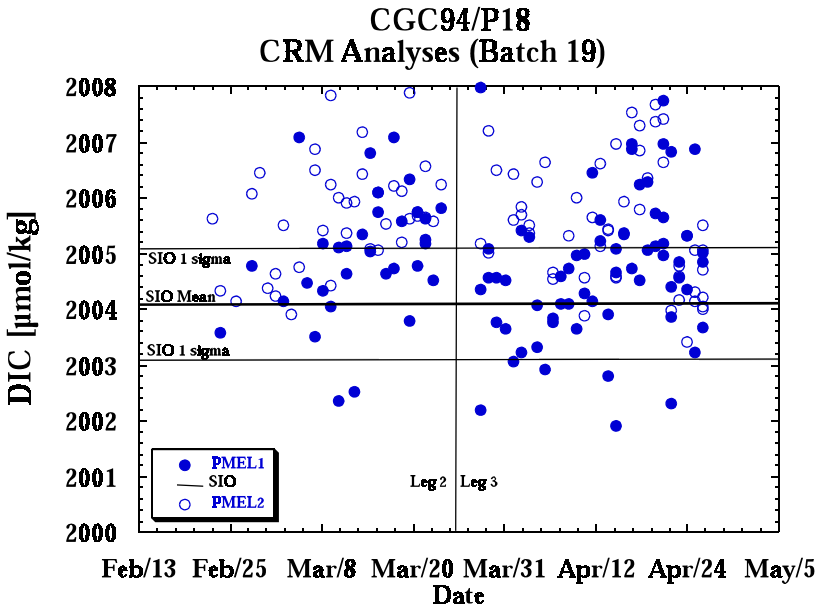

Fig. 2. CRM (Batch 19) analyzed during the eastern Pacific 1994 cruise. The overall uncertainty for both instruments combined was determined to be within ±1.4 µmol/kg DIC. Manometrically derived DIC = 2004.1 ± 1.0 µmol/kg (n=17).

Table 3. CRM (Batch 19) analyzed during the eastern Pacific 1994 cruise.

	PMEL-1 (µmol/kg)	Correction applied	PMEL-2 (µmol/kg)	Correction applied
Leg 2	2005.1 ± 1.9 (n = 35)	–1.0	2005.7 ± 0.9 (n = 39)	–1.6
Leg 3	2004.9 ± 1.5 (n = 67)	–0.8	2005.7 ± 1.3 (n = 54)	–1.6

Standard deviations are given at the 1σ level. The manometrically derived DIC = 2004.1 ± 1.0 µmol/kg.

Table 4. Precision of DIC analyses during the eastern Pacific 1994 cruise.

Station	Depth (m)	Precision (µmol/kg) Samples from different PVC bottles, same depth	Samples from same PVC bottle
T1	500	2301.6 ± 1.2 (n = 5)	2302.3 ± 1.0 (n = 5)
192	1000	2362.4 ± 0.4 (n =10)	2362.1 ± 0.9 (n = 10)

Values shown are for PMEL-1 and PMEL-2 combined. Standard deviations are given at the 1σ level.

Table 5. Relative error of duplicate data from PVC bottles tripped at 10 and 1000 m during the eastern Pacific 1994 cruise.

Depth (m)	*n*	Relative error (%)
10	101	0.015
1000	100*	0.013

*1 pair was omitted from statistical analysis. Values shown are for PMEL-1 and PMEL-2 combined.

Table 6. Long-term precision based on CRM analyses from 1990 to 1994.

Year	CRM Batch #	n	Precision (µmol/kg)
1990	1	26	±2.5
1991	No CRM available	—	—
1992S	10	68	±1.3
1992F	12	76	±1.5
1994	19	195	±1.3

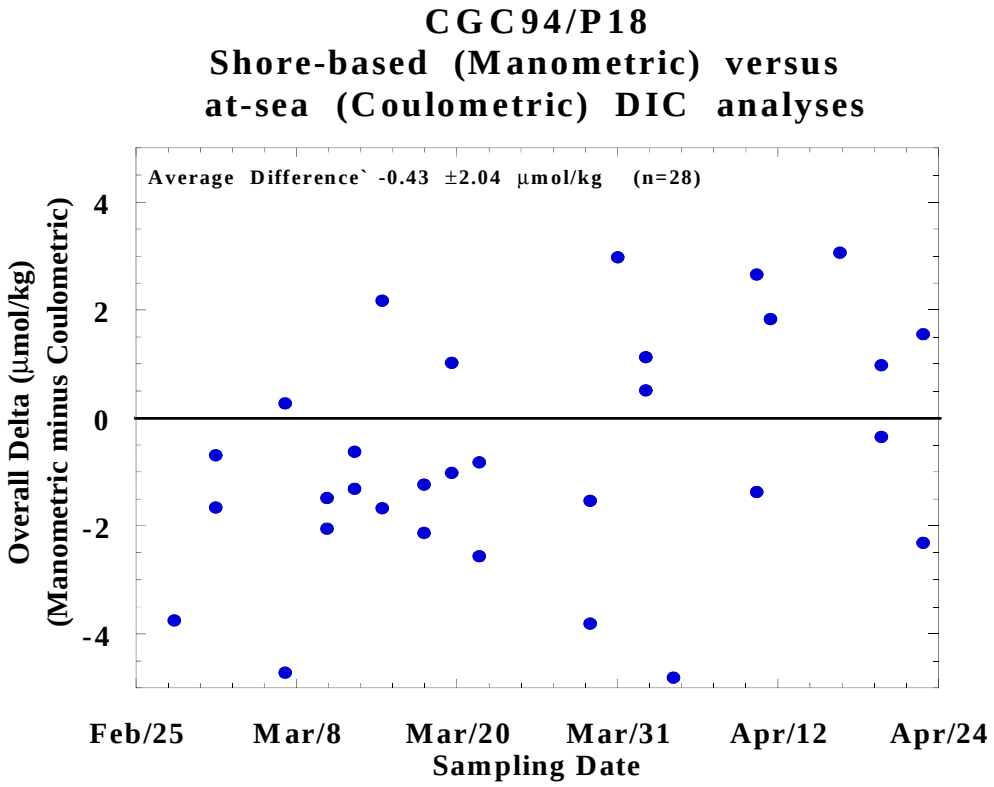

Fig. 3. Shore-based (manometric) versus at-sea (coulometric) DIC analyses during eastern Pacific 1994 cruise.

2.1.6 Total Alkalinity (TAlk)

Samples were taken from the same 500-mL Pyrex™ bottles used for DIC analyses, and were analyzed within 12 hours. The titration system used to determine TAlk consisted of a Metrohm 665 Dosimat™ titrator and an Orion™ 720A pH meter controlled by a personal computer (Millero *et al.*, 1993). The acid titrant, in a water-jacketed burette, and the seawater sample, in a water-jacketed cell, were kept at 25 ± 0.1°C with a Neslab™ constant-temperature bath. The plexiglass water-jacketed cells were similar to those used by Bradshaw *et al.* (1988), except that a larger volume (200 mL) was used to increase the precision. The cells had fill and drain valves with zero dead-volume, to increase the reproducibility of the cell volume.

The GWBASIC™ program used to run the titration recorded the volume of the added acid and the electromagnetic force (emf) of the electrodes using an RS232 interface. The titration was made by adding HCl to seawater past the carbonic acid endpoint. A typical titration records the emf reading after the readings stabilize (±0.09 mv), and adds enough acid to change the voltage to a preassigned increment (±13 mv). In contrast to the delivery of a fixed-volume increment of acid, this method results in an even distribution of data points throughout the titration curve.

The HCl solutions used throughout the cruise were made, standardized, and stored in 500-mL glass bottles in the laboratory for use at sea. The 0.25 M HCl solutions were made from 1 M Mallinckrodt™ standard solutions in 0.45 M NaCl to yield an ionic strength equivalent to that of

average seawater (0.7 M). The acid was independently standardized using a coulometric technique (Taylor and Smith, 1959; Marinenko and Taylor, 1968) by the University of Miami and by Dr. Dickson; the two standardization techniques agreed to ±0.0001 N.

The volumes of the cells used at sea were determined in the laboratory by weighing them filled with degassed Milli-Q™ water. The density of water at the temperature of the measurements (25°C) was calculated from the international equation of the state of seawater (Millero and Poisson, 1981). The nominal volumes of the cells were about 200 mL and the values were determined to ±0.03 mL. The reliability of the volumes was assessed by comparing the values of TAlk obtained for Gulf Stream seawater with open (weighed amounts of seawater) and closed cells using the same acid, electrodes, and Dosimat™. If the volume was correct, the TAlk from the open and closed cells should be the same. If the cells were modified during the cruise, adjustments were made to the volumes using the daily titrations on low-nutrient surface water and CRMs (Batch 19).

The volume of HCl delivered to the cell is traditionally assumed to have a small uncertainty (Dickson, 1981) and is equated with the digital output of the titrator. Calibrations of the Dosimat™ burettes with Milli-Q™ water at 25°C indicated that the systems deliver 3.000 mL (the value for a titration of seawater) to a precision of 0.0004 mL. This uncertainty resulted in an error of 0.4 µmol/kg in TAlk and DIC. The accuracy of the volume of acid delivered by the Dosimats™ was as much as ten times greater (4.0 µmol/kg).

Internal consistency of each cell was checked before, during, and after the cruise by titrating CRM Batch 19 prepared by Dr. Dickson; this was the same batch used for calibration of DIC. The TAlk of CRM Batch 19 was determined by open cell (weighed) titration in the laboratory prior to the cruise and was found to be 2251 µmol/kg (n = 9). A total of 114 CRM measurements were made at sea ($\bar{x}$ = 2254 ± 2 µmol/kg) on three different cells. The deviations from the mean at sea are shown in Fig. 4. All TAlk data have been corrected to laboratory CRM values for each cell and each leg.

2.1.7 $^{13}C/^{12}C$ *Isotopes* ($\delta^{13}C$)

Samples were collected from the PVC bottles in pre-washed and baked (450°C) 250- or 500-mL ground glass- stoppered bottles using a length of Tygon™ tubing. The tubing was flushed for a few seconds, the end of the tubing was then placed at the bottom of the upright sample bottle, and the bottle was filled, then overflowed by at least half its volume. Flow was stopped as the Tygon™ tubing was removed from the top of the bottle to avoid splashing.

Using a syringe or turkey baster, 10 to 20 mL were withdrawn from the top of the sample to lower the water level to approximately 1 cm below the neck of the bottle, avoiding backwash into the sample. The ground glass joint of the bottle was wiped dry with Kimwipes™, then 100 μL (per 250 mL of seawater) of a saturated $HgCl_2$ solution was injected into the sample using an Eppendorf™ pipette. The ground-glass stopper, which had been pregreased with Apiezon-M™ grease, was then inserted straight into the bottle without twisting. If any air streaks in the grease seal

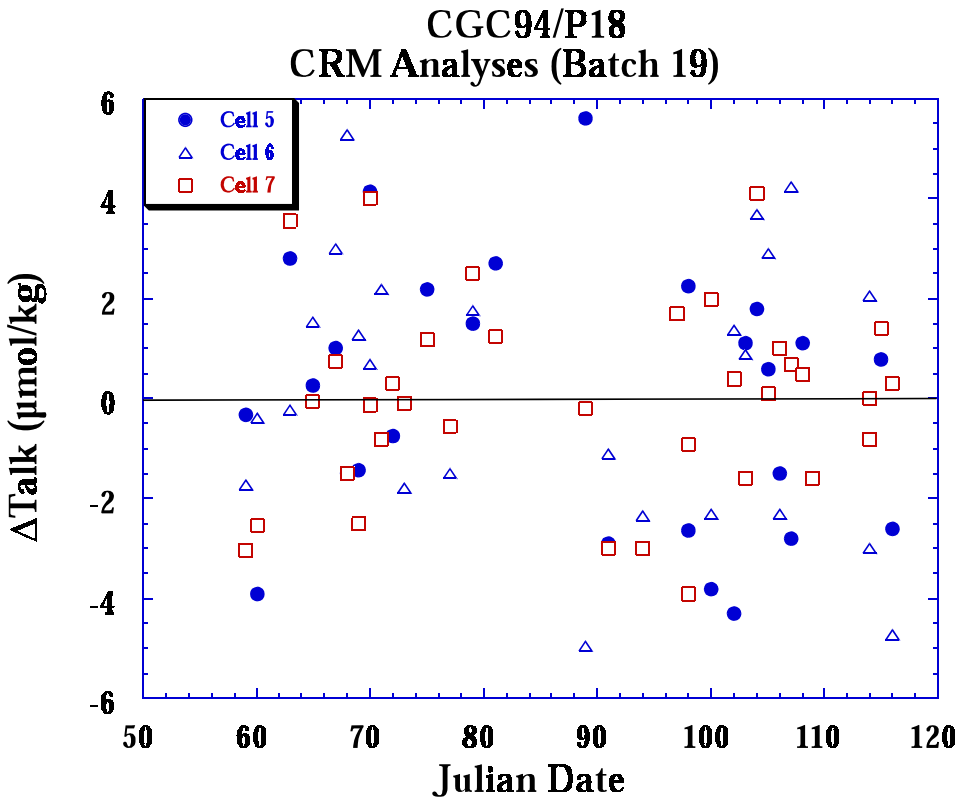

Fig. 4. Deviation from the mean for TAlk of CRM (Batch 19) during the eastern Pacific 1994 cruise.

were visible, the stopper was removed, cleaned, and regreased, then the bottle was resealed. Clips (if required for the bottle neck type) were placed on the necks of the bottles, and two heavy rubber bands were placed around the stopper and bottle to prevent leakage. The sample bottle was then overturned a few times to mix the $HgCl_2$ throughout the sample.

At the onshore laboratory, CO_2 was extracted from the DIC seawater sample using a modification of the He stripping technique of Kroopnick (1974), as described in Quay *et al.* (1992). The stripper comprised a glass tube with a stainless steel fitting and silicone-greased glass stopcock at the bottom (which connects to the He line), a glass frit through which the He passed, and a stainless steel fitting containing a 3-layer silicone rubber septum at the top. Approximately 1 mL H_3PO_4 was injected into the stripper and bubbled with He for 10 min. The gas was then evacuated from the stripper and the stripper weighed. 80 to 125 mL of the sample was then drawn into the stripper and weighed again to allow calculation of the weight of water analyzed. A stainless steel needle pierced the septum, connecting the stripper to the extraction line, which had been evacuated and filled with He. The sample was stripped with 99.997% pure He at a flow rate of about 200 ml/min for 20 min. Water was trapped out in two glass traps submerged in dewars containing a slush mixture of dry ice and isopropanol at –70°C. CO_2 was collected at –196°C in glass loop traps submerged in lN_2. The $\delta^{13}C$ was then measured on a Finnigan™ MAT 251 mass spectrometer.

The efficiency of the extraction method was 100% ± 0.5%, based on gravimetrically prepared Na_2CO_3 standards. The precision of the $\delta^{13}C$ analyses was ±0.02 per mil, based on replicate analyses of standards and seawater samples.

2.1.8 Nutrients

2.1.8.1 Sampling procedures and equipment; analytical methods. Nutrient samples were collected from the PVC bottles into aged 20-mL high-density polyethylene scintillation vials closed with Teflon™-lined polyethylene caps. All vials and caps were rinsed with 10% HCl and deionized water prior to each station, and rinsed at least three times with sample before filling. Samples were usually analyzed immediately after collection; however, some samples were stored for up to 12 hours at 4–6°C. An Alpkem™ RFA/2 autoanalyzer was used to determine dissolved concentrations of silicate ($Si(OH)_4$), phosphate (PO_4^{3-}), nitrate (NO_3^-), and nitrite (NO_2^-). Measurements were made in a temperature-controlled laboratory (21 ± 1°C). The following analytical methods were employed:

- $Si(OH)_4$ was converted to silicomolybdic acid and reduced with stannous chloride to form silicomolybdous acid or molybdenum blue (Armstrong, 1967).
- PO_4^{3-} was converted to phosphomolybdic acid and reduced with ascorbic acid to form phosphomolybdous acid in a reaction stream heated to 37°C (Bernhardt and Wilhelms, 1967).
- NO_2^- was diazotized with sulfanilamide and coupled with NEDA to form a red azo dye. ($NO_3^- + NO_2^-$) was measured by first reducing nitrate to nitrite in a copperized cadmium coil, and then analyzing for nitrite. NO_3^- was determined from the difference of ($NO_3^- + NO_2^-$) and NO_2^- (Armstrong, 1967).

2.1.8.2 Calibrations and standards. Standard materials for $Si(OH)_4$, NO_3^-, NO_2^-, and PO_4^{3-} were sodium fluorosilicate, potassium nitrate, sodium nitrite, and mono-basic potassium phosphate, respectively. Sodium fluorosilicate was referenced against a fused-quartz standard. Primary standards were prepared by dissolving standard material in deionized water, and working standards were prepared in low-nutrient seawater. At each station, seven concentrations of working standard were freshly prepared and analyzed prior to sample analysis, and the highest standard was again analyzed after the last sample. This allowed for regular monitoring of the response, drift, and linearity of the chemistry. All analyses were within the linear range of the instrument. Concentrations were converted to µmoles/kg by calculating sample densities using the laboratory temperature of 21°C and the practical salinity scale (UNESCO, 1981).

2.1.8.3 Precision. Analytical precision was determined by replicate measurements (usually 4–5 measurements) on 46 samples from depths greater than 100 m. The average standard deviations of these precision tests in µmol/kg was 1.1 $Si(OH)_4$, 0.015 PO_4^{3-}, and 0.22 NO_3^-; the average percent deviations were 0.56% $Si(OH)_4$, 0.84% PO_4^{3-}, and 0.59% NO_3^-.

2.1.9 Total Organic Carbon (TOC) and Nitrogen (TON)

Water samples taken for organic carbon and nitrogen determinations were not filtered, hence total organic carbon (TOC) and nitrogen (TON) were measured. Samples for TOC and TON analysis were collected using the PVC bottles on the CTD rosette (data in Appendix A), or with 10- or 20-L GoFlo™ bottles deployed on a Kevlar™ line (data in Appendix B). TOC samples were collected in 40-mL EPA vials with Teflon™-lined closures (I-Chem Research). Vials and caps were rinsed three times, filled 3/4 full, immediately acidified with 150 µL of 50% (v/v) H_3PO_4 and stored in the dark. Analyses were completed 6–9 months after collection. TON samples were collected in acid-washed 125-mL polyethylene bottles. Bottles and caps were rinsed three times, filled 3/4 full, and frozen (–20°C) for later onshore analysis. A comparison of TOC concentrations in the frozen TON samples and the acidified, dark-stored samples showed no discernible differences.

2.1.9.1 TOC analyses. All TOC samples were analyzed by high-temperature combustion using a non-commercial system modified from the system of Hansell (1993). A quartz combustion tube (490 mm × 13 mm) was packed with platinum pillows (Ionics, Inc.), Cuprox™ (Leeman Labs), and Sulfix™ (Wako Pure Chemical Industries, Inc.). Four pillows were placed 11 cm from the top of the tube. Below the pillows were 15 g of Cuprox™ and then 15 g of Sulfix™. The pillows, Cuprox™, and Sulfix™ were each separated by a thin layer of quartz wool. The packing material was supported from below by a platinum screen (one of the pillows unfolded), which in turn was supported by a quartz rod (0.6 mm O.D.) extending to the bottom of the column. The combustion column was maintained at 700°C in a Thermolyne™ 21100 tube furnace. The samples were sparged of inorganic carbon with Ultra-Pure™ O_2. Carbon dioxide generated from 100-µL injections was detected using a LICOR™ Model LI-6252 NDIR analyzer operated in the absolute mode. Data were acquired on a Macintosh computer running Dynamax Macintegrator™ 1.3 software (Rainin Instruments, Inc.).

Calibrations were performed daily with a 4-point standard curve using glucose in Milli-Q™ water (0–100 µmol/L C). The system blank (normally 7–8 µmol/L C) was determined using vialed Milli-Q™ water produced at BBSR. The organic carbon content of this water (3 µmol/L C) was determined by intercomparison with the low-carbon water used by Carlson and Ducklow (1995). Vialed seawater, collected from 2600 m at the U.S. JGOFS Bermuda Atlantic Time-Series Study site in the Sargasso Sea, was also analyzed each day to help monitor the system blank and the behavior of the analyzer. The percent relative standard deviation (RSD) for all TOC samples at depths >1000 m, with a mean concentration of 39.9 µmol/L, was 7.8%. In the surface layer, the RSD for TOC was approximately 4%.

2.1.9.2 TON analyses. Concentrations of TON were determined by UV photooxidation according to the method described by Walsh (1989). Frozen samples were thawed by placing sample bottles in a warm water bath. A 10-mL aliquot was removed from each sample bottle and placed in a 20-mL fused quartz tube equipped with a ground stopper (Quartz Scientific, Inc.). Fifty µL of 30% hydrogen peroxide was added to each tube and placed in a homemade irradiation unit overnight

(17–20 hours). Tests for the recovery of known compounds, such as glycine, showed that inconsistent results were obtained with shorter irradiation periods. The irradiation unit contained a 1200W UV lamp (Hanovia) protected by a quartz jacket. A 2-tier aluminum tube holder (40 tubes total) fitted around the lamp and held the samples 8 cm from the lamp. A fan at the bottom of the unit cooled the samples. A hinged aluminum cylinder, open at the top and bottom, was fitted around the samples to keep stray UV light from leaving the system. This entire unit was placed in a fume hood, the front of which was covered with a black curtain while in use (again to collect stray UV light).

After irradiation, aliquots of the samples (which were refrigerated overnight) that had not been oxidized, and the photooxidized aliquots, were analyzed for nitrate plus nitrite using a colorimetric method on a Technicon™ Autoanalyzer II (Knap *et al.*, 1993). Daily calibration was achieved from 4-point calibration curves using both KNO_3 and KNO_2. Cadmium column efficiency was determined by comparing the slope of the NO_3^- calibration curve with the slope obtained from the NO_2^- calibration curve. Due to the photoreduction of NO_3^- to NO_2^- (Walsh, 1989), it is imperative that the cadmium column be efficient when analyzing samples containing high concentrations of NO_3^-. Therefore, a new column (efficiency >98%) was employed when analyzing NO_3^- samples >10 µmol/L. The column efficiency was generally >90% when running the low-NO_3^- samples. Low-nutrient seawater (Sargasso Sea surface water) was always processed with the samples as a daily quality control. TON in the deep ocean is calculated as the difference between two large numbers (total inorganic nitrogen and total dissolved nitrogen, including inorganic and organic fractions), hence high precision in the deep ocean has been an elusive goal. The RSD for all TON samples >1000 m, with a mean concentration 2.5 µmol/L N, was 18%. In the surface layer, where inorganic nitrogen was non-detectable, the RSD for TON was approximately 4%.

2.1.10 Salinity

Salinity samples were collected in 125-mL amber glass bottles directly from the PVC bottles; care was taken not to touch the petcock. Analysis was conducted with two Guildline™ model 8400A inductive autosalinometers, standardized with IAPSO Standard Seawater, batch P114, and located in a temperature-controlled van. The autosalinometer in use was standardized before each run, and either at the end of each run or after no more than 48 samples. Drift between standardizations was monitored and individual samples were corrected by linear interpolation. Duplicate samples taken from the deepest bottle on each cast were analyzed on a subsequent day. Bottle salinities were compared with preliminary CTD salinities to aid in identification of leaking bottles as well as to monitor the CTD conductivity cells' performance and drift.

The expected precision of the autosalinometer with an accomplished operator is 0.001, with an accuracy of 0.003. To assess the precision of discrete salinity measurements on this cruise, a examination was made of data from instances in which two bottles were tripped within 1 m of each other at the same station below a depth of 2000 m. For the 138 occasions on which both bottles of

the pair had acceptable salinity measurements, the standard deviation of the differences was 0.0012. This value is very close to the expected precision.

2.1.11 Beam attenuation due to particles (c_p)

A 25-cm-pathlength Sea Tech™ transmissometer was interfaced with the CTD. The 0–5 volt output (V) is proportional to beam transmission (T), i.e., $T = V/5$ (or T*100 when expressed as percent transmission). Data were acquired at the same rate as other CTD parameters and were de-spiked and bin-averaged at 1-db intervals. Beam transmission was converted to beam attenuation coefficients using $c = -(\ln T)/z$, where c = the beam attenuation coefficient (m^{-1}), z = beam path length (m), and T = beam transmission. Beam attenuation is linearly related to particle concentration (given a uniform particle-size distribution and index of refraction) whereas beam transmission is not.

When possible, we filtered water through preweighed filters so we could gravimetrically determine the concentration of particulate matter (PM) through the water column for a correlation with beam attenuation (e.g., Gardner *et al.*, 1995). As this was not possible for this transect, we used the following steps for data reduction. The minimum c for each profile was determined and plotted. The depth of the minimum was generally between 2000 and 3000 m. Each profile was examined for anomalous data; only 2 of the profiles had to be eliminated. The transmissometer was not on the CTD for 17 profiles. Successive plots of c were compared, and where the minimum c differed from surrounding plots by more than 0.001 m^{-1}, a linear shift was made in the profile so that c at 2000 m was the same as in adjacent profiles. This procedure corrects for incomplete cleaning of the optical windows and errors in air calibration.

Beam attenuation is the sum of attenuation due to water (c_w), particles (c_p), and dissolved colored organic matter (c_y). In the open ocean the value of c_y is negligible. Sea Tech™ transmissometers were factory-calibrated to have a c of 0.364 m^{-1} in particle-free water, but generally require empirical calibrations by water filtration. Because no filter-calibration data were available, the cruise minimum c was used for c_w; this constant was subtracted from each profile. The remaining value is c_p, attenuation due to particles in the water.

2.2 Biological Cast Operations

In addition to the CTD casts, samples were collected using 10- or 20-L GoFlo™ bottles deployed on a Kevlar™ line (Table 7) to assess the biological components of the carbon species in the upper 200–300 m of the water column. These included estimates of biomass (chlorophyll-*a*, phaeopigments, and biogenic silica) and primary productivity. A more comprehensive listing of the biological data is available through MBARI (Michisaki *et al.*, 1996). Samples for TOC and TON were also collected from some of the biology casts.

2.2.1 Methods and Materials

Water for the productivity experiments was collected at six fixed depths representing 100, 50, 30, 15, 5, and 1% of the surface irradiance (S.I.) as determined with a Secchi disk. Dedicated, Teflon-coated Go-Flo™ bottles lowered on a Kevlar™ cable and closed with Teflon™ messengers were employed. The sampling system and cleaning of components, as well as bottle handling and filtration, were modeled after the recommendations of Fitzwater *et al.* (1982). In addition to samples from the Kevlar™ casts, measurements of chlorophyll-a and phaeopigments were made on samples collected in the upper 200 m with the rosette sampler on the CTD. (Appendix A).

2.2.2 Chlorophyll-a and Phaeopigments

Chlorophyll-*a* and phaeopigments were determined by the fluorometric technique using a Turner™ Designs Model 10-005 R fluorometer calibrated with commercial chlorophyll-*a* (Sigma). Samples for determination of plant pigments were filtered onto 25-mm Whatman™ GF/F glass fiber filters and extracted in 90% acetone in a freezer for between 24 and 30 hours (Venrick and Hayward, 1984). Other than the modification of the extraction procedure, the method used is the conventional fluorometric procedure of Holm-Hansen *et al.* (1965) and Lorenzen (1966). Additional samples were also filtered onto 0.2-, 1.0-, and 5.0-µm-pore Nuclepore™ membrane filters.

2.2.3 Primary Productivity

The stable isotopes ^{13}C and ^{15}N (Hama *et al.*, 1983; Slawyk *et al.*, 1984), rather than the radioactive isotope ^{14}C, were used to measure primary production. Samples were drawn into 1-L polycarbonate bottles which had been washed using the Fitzwater *et al.* (1982) procedure; this method was also used for cleaning the Go-Flo™ bottles. For carbon measurements, Na_2CO_3 (minimum 99.9%; Cambridge, US) was added to reach a concentration of 7.2% of the total inorganic carbon in the ambient seawater (Kanda *et al.*, 1985). An initial sample was inoculated with the tracer and filtered immediately with no incubation to determine abiotic particulate ^{13}C incorporation and initial isotopic ratio. The bottles were encased in nickel screens (Perforated Products) that acted as neutral density filters to reduce light intensity to the level at the depth from which the sample was collected, and were incubated on deck in surface seawater-cooled Plexiglas incubators. All samples were incubated for either 6 (dual-labeled with ^{13}C and ^{15}N) or 24 (^{13}C only) hours under natural light; however, samples were collected and incubations started at various times of the day. For determination of particulate carbon fixation, the water from the bottles was filtered onto Whatman™ GF/F filters at <250 mm mercury. The filters were dried at 60°C and stored in a desiccator for later analysis ashore on a Europa™ mass spectrophotometer. The calculation of production follows the rationale of Dugdale and Wilkerson (1986) for ^{15}N, as described in Chavez *et al.* (1996).

Table 7. Biology cast locations and dates during the eastern Pacific 1994 cruise.

Station	Latitude			Longitude			Date
8	53°	22.9′	S	76°	22.4′	W	23 Feb 94
9	61°	12.7′	S	90°	11.2′	W	25 Feb 94
10	67°	0.0′	S	103°	0.0′	W	27 Feb 94
13	65°	30.0′	S	103°	0.0′	W	28 Feb 94
16	63°	58.0′	S	103°	2.0′	W	1 Mar 94
19	62°	30.0′	S	103°	0.0′	W	2 Mar 94
23	60°	30.0′	S	103°	0.0′	W	3 Mar 94
26	59°	0.0′	S	103°	0.0′	W	4 Mar 94
27	58°	30.0′	S	103°	0.0′	W	5 Mar 94
30	56°	30.0′	S	103°	0.0′	W	7 Mar 94
33	54°	29.7′	S	102°	58.9′	W	8 Mar 94
36	52°	30.0′	S	103°	0.0′	W	9 Mar 94
40	49°	50.0′	S	103°	0.0′	W	10 Mar 94
43	48°	0.0′	S	103°	0.0′	W	11 Mar 94
47	46°	0.0′	S	103°	0.0′	W	12 Mar 94
51	44°	0.0′	S	103°	0.0′	W	13 Mar 94
55	42°	0.0′	S	103°	0.0′	W	14 Mar 94
58	40°	30.0′	S	103°	0.0′	W	15 Mar 94
62	38°	30.0′	S	103°	0.0′	W	16 Mar 94
66	36°	30.0′	S	103°	0.0′	W	17 Mar 94
70	34°	30.0′	S	103°	0.0′	W	18 Mar 94
74	32°	30.0′	S	103°	0.0′	W	19 Mar 94
78	30°	30.0′	S	103°	0.0′	W	20 Mar 94
81	29°	0.0′	S	103°	0.0′	W	21 Mar 94
84	27°	30.0′	S	103°	0.0′	W	22 Mar 94
90	24°	29.3′	S	103°	0.0′	W	29 Mar 94
94	26°	30.0′	S	103°	0.0′	W	30 Mar 94
98	20°	0.0′	S	103°	0.0′	W	31 Mar 94
101	18°	53.7′	S	103°	8.5′	W	1 Apr 94
104	17°	30.0′	S	103°	0.0′	W	2 Apr 94
108	15°	30.0′	S	103°	0.0′	W	3 Apr 94
112	13°	30.0′	S	103°	0.0′	W	4 Apr 94
115	12°	0.0′	S	103°	0.0′	W	5 Apr 94
119	10°	0.0′	S	103°	0.0′	W	6 Apr 94
122	8°	51.3′	S	104°	41.6′	W	7 Apr 94
126	7°	18.4′	S	106°	57.3′	W	8 Apr 94
130	5°	46.5′	S	109°	12.7′	W	10 Apr 94
133	4°	29.8′	S	110°	19.5′	W	10 Apr 94
137	2°	40.0′	S	110°	20.0′	W	11 Apr 94
141	1°	20.0′	S	110°	20.0′	W	12 Apr 94
145	0°	0.0′	S	110°	19.0′	W	13 Apr 94
149	1°	20.0′	N	110°	20.0′	W	14 Apr 94
153	2°	40.0′	N	110°	20.0′	W	15 Apr 94
157	4°	30.0′	N	110°	20.0′	W	16 Apr 94
160	6°	0.0′	N	110°	20.0′	W	17 Apr 94

Table 7. (continued)

Station	Latitude			Longitude			Date
164	8°	0.0′	N	110°	20.0′	W	18 Apr 94
168	10°	9.1′	N	110°	0.4′	W	19 Apr 94
172	12°	40.3′	N	109°	59.9′	W	20 Apr 94
175	14°	29.7′	N	110°	0.1′	W	21 Apr 94
179	16°	30.0′	N	110°	0.0′	W	22 Apr 94
183	18°	30.0′	N	110°	0.0′	W	23 Apr 94
188	21°	0.0′	N	110°	0.0′	W	24 Apr 94
192	22°	43.9′	N	110°	0.0′	W	25 Apr 94

2.2.4 Biogenic Silica

Biogenic silica depth profiles were taken at most biology stations, depending on availability of water. Depths correspond to the depths utilized for uptake rate experiments. One-L samples were filtered onto 47-mm, 0.8-µm polycarbonate filters. The filters were frozen (−20°C) on board and taken back to the lab for analysis. Dissolution was carried out at 85°C in 0.5% Na_2CO_3 and the sample was acidified before silicate concentration was determined following the spectrophotometric method outlined in Parsons *et al.* (1984). There were no replicate analyses; however, based on similar measurements for the equatorial Pacific, precision was estimated at ±14%.

3. DATA TABLES

3.1 CTD Casts

A complete listing of the CTD data is available through NOAA (MCTaggart *et al.*, 1996). Discrete data are reported at all observed depths and are listed in this report as separate tables in Appendix A. Where no data are available, a null value (−9) has been inserted. Sample ID consists of the cast number followed by the 2-digit rosette position. Quality control flags follow the WHP Data Reporting Requirements (WOCE, 1994), and are listed in Tables 8 and 9. In Appendix A, the quality control flags are posted adjacent to the following parameters: Sample ID (flag indicates PVC sample bottle quality (Table 8)), CTD salinity, bottle salinity, nutrients, CFCs, DO, pCO_2, DIC, pH, and TAlk (flags indicate water quality for samples (Table 9)). In the electronic version, quality flags are posted adjacent to all parameters with the exception of pressure, in situ temperature, and potential temperature. Temperatures are reported using the ITS90 scale (Saunders, 1990). Sigma-theta (σ_θ) and potential temperature (θ) values in the tables were calculated using standard UNESCO algorithms (Fofonoff and Millard, 1983); input parameters include salinities and in situ temperatures, both from the CTD. To obtain an electronic version of the database by remote access, please see page iii of this report.

3.2 Biological Casts

Discrete bottle data for the biological parameters obtained from the Kevlar™ casts are presented in Appendix B. In both Appendix B and the electronic version of the biology casts quality flags are posted adjacent to the corresponding parameters. To obtain the database by remote access, please see page iii of this report.

Table 8. WOCE quality flag definitions for water bottles.

Flag	Definition
1	Bottle information unavailable
2	No problems noted
3	Leaking
4	Did not trip correctly
5	Not reported
7	Unknown problem
9	Samples not drawn from this bottle

A more detailed listing of water bottle quality flags of 3 or 4, as documented on the deck logs, are contained in a file available by contacting bullister@pmel.noaa.gov.

Table 9. WOCE water quality flag definitions.

Flag	Definition
1	Sample drawn but analysis not received
2	Acceptable measurement
3	Questionable measurement
4	Bad measurement
5	Not reported
6	Mean of replicate measurements
7	Manual chromatographic peak measurements
8	Irregular digital chromatographic peak integration
9	Sample not drawn for measurement

4. ACKNOWLEDGMENTS

The assistance of the officers and crew of the NOAA Ship *Discoverer* is gratefully acknowledged. The authors also wish to thank Ryan Whitney and Martha Jackson for manuscript preparation. Jim Gendron, also of PMEL, is acknowledged for formatting the data tables. We thank Drs. James F. Todd and David Goodrich of the NOAA Office of Global Programs. This research was supported by the Climate and Global Change Program of NOAA.

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APPENDIX A

TABULATED DISCRETE BOTTLE DATA (CTD CASTS)

APPENDIX B

TABULATED DISCRETE BOTTLE DATA (BIOLOGICAL CASTS)

The data presented in this report is available on a computerized Remote Bulletin Board System (RBIS), Internet FTP, and the World Wide Web (WWW). For information regarding electronic access to the data sets contact:

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Contoured sections of the data are also available at http://www.pmel.noaa.gov/CO2/

The evaluation of the CGC94 dissolved oxygen, nutrients, and CFC measurements by the WOCE Data Quality Experts and WOCE Hydrographic Office has not been completed. After completion of this process, revised versions of these data will be available from the WOCE Hydrographic Office, or by contacting bullister@pmel.noaa.gov.