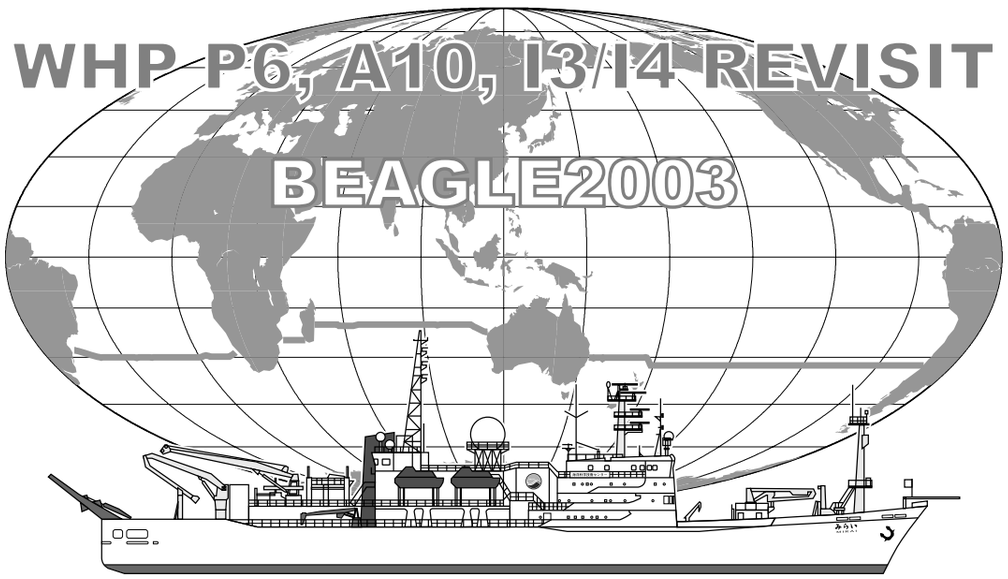
# WHP P6, A10, I3/I4 REVISIT DATA BOOK

## Blue Earth Global Expedition 2003 (BEAGLE2003)

**Volume 3**



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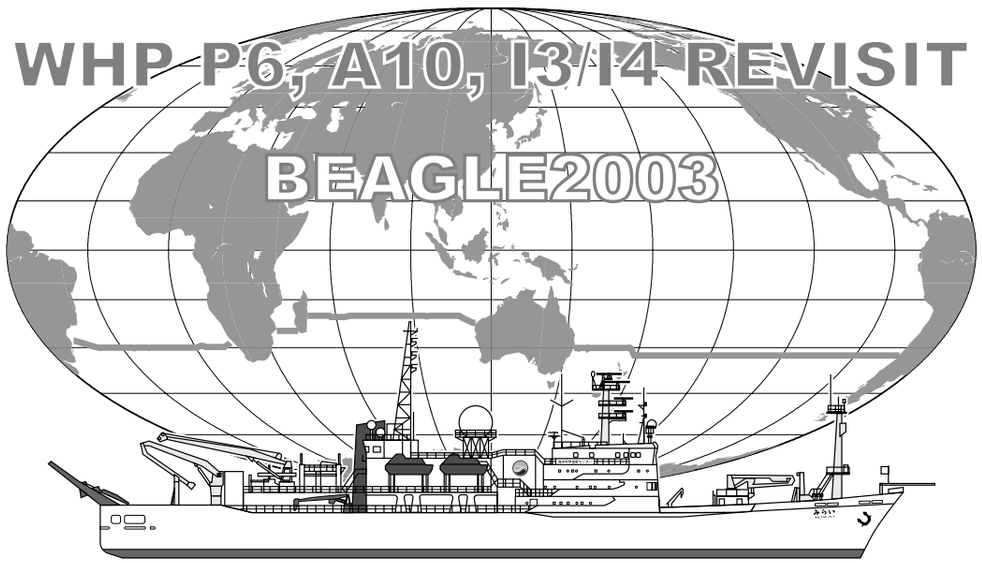
*Edited by*

*Yuichiro Kumamoto (JAMSTEC),*

*Shuichi Watanabe (JAMSTEC)*



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Volume 3

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# Contents (Volume 3)

# 3. Hydrographic Measurement Techniques and Calibrations (continued from Volume 2)

## 3.9 Chlorofluorocarbons (CFCs)

*7 December 2006*

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**(2) Introduction**

Chlorofluorocarbons (CFCs) are completely man-made gasses that are chemically and biologically stable gasses in the environment. The CFCs have been accumulated in the atmosphere since 1930's (Walker et al., 2000) and the atmospheric CFCs can slightly dissolve in sea surface water. The dissolved CFC concentrations in sea surface water should have changed year by year and then penetrated into the ocean interior by water circulation. Three chemical species of CFCs, namely CFC-11 ($CCl_3F$), CFC-12 ($CCl_2F_2$) and CFC-113 ($C_2Cl_3F_3$), dissolved in seawater are useful transient tracers for the ocean circulation with time scale on the order of decades.

In this cruise, we determined the concentrations of these CFCs in seawater on board.

**(3) Apparatus**

Dissolved CFCs were measured by a method modified from the original design of Bullister and Weiss (1988). Two systems were used for CFCs measurement. A custom made purging and trapping system was attached to gas chromatograph (GC-14B: Shimadzu Ltd) having an electron capture detector (ECD-14: Shimadzu Ltd). Porapak T® filler was packed in a 1/8" stainless steel trap column. PoraPlot Q-HT capillary columns [i.d.: 0.53mm, length: 2m, film layer thickness: 20$\mu$m] was used as a pre-column. PoraPlot Q-HT capillary columns [i.d.: 0.53mm, length: 20m, film layer thickness: 20$\mu$m] was used as a main analytical column in leg 1 and 2. The main analytical column was replaced by PoraBond Q capillary columns [i.d.: 0.53mm, length: 25m, film layer thickness: 10$\mu$m] in legs 4 and 5.

The change in main analytical columns has been due to serious problems found in the columns used in legs 1 and 2. The main columns used in legs 1 and 2 were clogged by particles peeled from column wall and carrier gas could not flow sufficiently. This problem affected to separation of compounds and analytical time.

**(4) Shipboard measurement**

*Sampling*

Seawater sub-samples for CFCs measurement were collected from 12 litter Niskin bottles to 300ml sub-sampling glass bottles which were developed for CFCs analyses in JAMSTEC. The sub-sampling bottles have stainless steel union altered from original design of Swagelok® on the top. A 1/4" $\phi$ stainless steel tube goes through the union into the bottle interior and reaches to near the bottom of bottle. A small plastic stop valve was on the upper tip of stainless steel tube. The bottles were filled by nitrogen gas before sampling. The valve was connected to Niskin bottle. The sub-sampling bottles were filled by seawater sample from the bottom. Two times of the bottle volumes of seawater sample were overflowed from vent valve put on side of the union and then the all valves closed from downstream. The bottles filled by seawater sample were kept in water bathes roughly controlled on sample temperature. The CFC concentrations were determined as soon as possible after sampling. These procedures were needed in order to minimize contamination from atmospheric CFCs.

*Analysis*

The CFCs analytical system is modified from the original design of Bullister and Weiss (1988). Constant volume of sample water is taken into the purging & trapping system. The volume of sample was 150 ml in legs 1 and 2 and 100 ml in legs 4 and 5. Dissolved CFCs are de-gassed by $N_2$ gas purge and concentrated in a 1/8" SUS packed trap column (Porapak T) cooled to –40 degree centigrade. The CFCs are desorbed by electrically heating the trap column to 130 °C, and lead into the pre-column. CFCs and other compounds are roughly separated in the pre-column and the compounds having earlier retention time than CFC-113 are sent to main analytical column. And then the pre-column is flushed buck by counter flow of pure nitrogen gas (Back flush system). The back flush system is prevent to enter any compounds that have higher retention time than CFC-113 into main analytical column and permits short time analysis. CFCs which are sent into main column are separated further and detected by an electron capture detector (ECD).

In legs 1 and 2, temperature rising analysis has been used because of too long of retention times of CFCs to use temperature constant analysis. The long retention time was due to problems on main analytical column mentioned above.

In legs 4 and 5, we can use temperature constant analysis due to applying new column for main analytical column. Analytical conditions are listed in Table 3.9.1.

Gas loops that the volumes were around 1, 3 and 10 ml were used for introducing standard gases into the analytical system.

Table 3.9.1. Analytical conditions of dissolved CFCs in seawater.

| | |
|---|---|
| *Leg 1* | |
| Temperature | |
| Analytical Column: | 70 or 100 °C constant for 10 minutes followed by temperature changing stage in 10 °C/min of the rate to 140 °C. |
| Detector (ECD): | 200 or 250 °C |
| Trap column: | –45 °C (at adsorbing) & 130 °C (at desorbing) |
| Mass flow rate of nitrogen gas (99.9999%) | |
| Carrier gas: | 3 - 7 ml/min |
| Detector make-up gas: | 17 ml/min |
| Back flush gas: | >10 ml/min |
| Sample purge gas: | 100 ml/min |
| *Leg 2* | |
| Temperature | |
| Analytical Column: | 75 °C constant for 5 minutes followed by temperature changing stage in 20°C/min of the rate to 130 °C. |
| Detector (ECD): | 270 or 290 °C |
| Trap column: | –45 °C (at adsorbing) & 130 °C (at desorbing) |
| Mass flow rate of nitrogen gas (99.9999%) | |
| Carrier gas: | 8 - 9 ml/min |
| Detector make-up gas: | 16 - 21 ml/min |

Table 3.9.1. continued

| | |
|---|---|
| Back flush gas: | 4 - 7 ml/min |
| Sample purge gas: | 200 ml/min |

*Legs 4 and 5*

Temperature

| | |
|---|---|
| Analytical Column: | 95 °C constant. |
| Detector (ECD): | 290 °C |
| Trap column: | –45 °C (at adsorbing) & 130 °C (at desorbing) |

Mass flow rate of nitrogen gas (99.9999%)

| | |
|---|---|
| Carrier gas: | 27 ml/min |
| Detector make-up gas: | 28 ml/min |
| Back flush gas: | >15 ml/min |
| Sample purge gas: | 300 ml/min |

Standard gas (Taiyo Toyo Sanso co. ltd.) in all legs

| | |
|---|---|
| Base gas: | Nitrogen |
| CFC-11: | 850 ppt (v/v) |
| CFC-12: | 500 ppt (v/v) |
| CFC-113: | 90 ppt (v/v) |

**(5) Quality control**

Analytical conditions of CFCs have been changed among legs. Data qualities are mentioned for each leg.

*Legs 1*

One of two analytical systems had serious problem in cold trap heating system. We needed considerable time for repairing the problem and we could not obtain CFCs data in around half of planed stations. Another system also had some problems in the analytical columns. It was closed by the resins and considerable high pressure of carrier gas had been needed to obtain the mass flow rate of 5 ml/min. Additionally, the column cannot separate CFC-11 peak from unknown interference peaks. Almost all CFC-11 data was bad in the quality and flag was “4”. Considerable numbers of CFC-12 and -113 data were also not good in quality due to unstable condition of analytical systems and were given flag of “4”.

*Legs 2*

Before starting leg 2, analytical conditions have been coordinated again. The peaks of CFC-11 and -113 cannot separate from unknown interference peaks. Separation of CFC-12 peak was better than that in leg 1. Most CFC-12 data was good in quality and given flag of “2”. The analytical precision was estimated from replicate sample analysis of CFC-12. The precision was estimated from average of absolute difference to be 0.009 $\pm$ 0.011 pmol/kg (n = 24).

*Legs 4*

We got new analytical columns at before Leg 3 that did not have plan for CFCs analyses. During Leg 3, we have tested the columns and successfully decided the analytical condition for CFC-11 and 12. CFC-113 however had been interfered by unknown large peak. We tried to calculate CFC-113 peak by post analyses of the chromatogram and gave the data flag “4”. In the case of that the CFC-113 peak had completely been covered by interference peaks, we could not calculate the area of peak and given the data flag “5”. The analytical precisions

are estimated from replicate sample analyses for CFC-11 and -12. The precisions were estimated from average of absolute difference to be 0.012 ± 0.013 (n = 98) and 0.007 ± 0.008 pmol/kg (n = 98) for CFC-11 and -12, respectively.

*Legs 5*

Analytical conditions were same as that in leg 4. In the one of the analytical systems, serious problem has been found in several stations of this leg. The problem was considerable high blank for CFC-12 chromatogram peak. We could not find the causes of the problems by end of this leg. The problems interfered in determination of CFC-12. This problem was remarkable in 5 stations namely stations of I03-557, I03-480, I03-455, I03-451 and I03-447. Although we tried to correct the blank, quality of the data is not good. CFC-12 data in these stations had been given flag of "4". In CFC-113 analyses, there are same problems as that of leg 4 and almost all quality flags were "4". The precisions were estimated from average of absolute difference to be 0.009 ± 0.010 pmol/kg (n = 131) and 0.006 ± 0.006 pmol/kg (n = 122) for CFC-11 and -12, respectively.

*Standard Gasses*

Standard gasses used in this cruise have been made by Taiyo Nissan Co. Ltd. CFC mixing ratios of the standard gases have been determined by the maker using gravimetric method. The standard gases used in this cruise have not been calibrated to SIO scale standard gases yet because SIO scale standard gasses is hard to obtain due to legal difficulties for CFCs import into Japan. The data will be corrected as soon as possible when we will obtain the standard gasses.

*Blank correction*

CFCs concentrations in deep water which was one of oldest water masses of the ocean were low but not zero for CFC-11 and -12. In leg 2, Average concentrations of CFC-12 in water samples collected from density range of 27.5 - 27.8 sigma-theta were 0.009 ± 0.004 (n = 226). Average concentrations of CFC-11 and -12 in water samples collected from density range of sigma-theta > 27.8 and sigma-4 < 45.87 were 0.029 ± 0.005 (n = 195), 0.011 ± 0.003 (n = 195) in leg 4 except data from western region where relatively new deep water mass could come by western boundary current (on Santos Plateau and Vema Channel). Average concentrations of CFC-11 and -12 in water samples collected from density range of sigma-theta > 27.76 and sigma-4 < 45.87 were 0.021 ± 0.006 (n = 251), 0.011 ± 0.003 (n = 243) in leg 5 except data from I04 section where relatively new deep water mass could come (on Mozambique Basin). These values would be sampling blanks which was contaminations from Niskin bottle and/or during sub-sampling and were subtracted from all measurements.

**(6) References**

Walker, S.J., Weiss, R.F. and Salameh, P.K., Reconstructed histories of the annual mean atmospheric mole fractions for the halocarbons CFC-11, CFC-12, CFC-113 and Carbon Tetrachloride, Journal of Geophysical Research, 105, 14,285-14,296, (2000).

Bullister, J.L and Weiss, R.F. Determination of $CCl_3F$ and $CCl_2F_2$ in seawater and air. Deep Sea Research, 35, 839-853 (1988).

## 3.10 $\delta^{13}C$ and $\Delta^{14}C$ of Dissolved Inorganic Carbon

*25 December 2006*

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**(2) Introduction**

Stable and radioactive carbon isotopic ratios ($\delta^{13}C$ and $\Delta^{14}C$) of dissolved inorganic carbon (DIC) are good tracers for the anthropogenic carbon in the ocean. During MR03-K04 cruise, named BEAGLE2003, we collected seawater samples for $\delta^{13}C$ and $\Delta^{14}C$ analyses at stations along the WOCE-P6 (Leg-1&2), WOCE-A10 (Leg-4), and WOCE-I3&I4 (Leg-5) lines in the southern hemisphere. Here we report the final results of $\delta^{13}C$ and $\Delta^{14}C$ of DIC. Our preliminary reports of $\delta^{13}C$ and $\Delta^{14}C$ measurements are replaced by this final report. General information and other hydrographic data of BEAGLE2003 cruise have already published in our previous data books of BEAGLE2003 (Uchida and Fukasawa, 2005a,b)

**(3) Sample collection**

The sampling stations are summarized in Figure 3.10.1 and Table 3.10.1-4. A total of 3,060 seawater samples, including 233 replicate samples, were collected between surface (about 10 m depth) and near bottom at 97 stations using 12-liter X-Niskin bottles. The seawater in the X-Niskin bottle was siphoned into a 250 $cm^3$ glass bottle with enough seawater to fill the glass bottle 2 times. Immediately after sampling, 10 $cm^3$ of seawater was removed from the bottle and poisoned by 50 $\mu$l of saturated $HgCl_2$ solution. Then the bottle was sealed by a glass stopper with Apiezon M grease and stored in a cool and dark space on board. Theses procedures on board basically follow the methods described in WOCE Operation Manual (McNichol and Jones, 1991).

**(4) Sample preparation**

In our laboratory, DIC in the seawater samples were stripped cryogenically and split into three aliquots: Accelerator Mass Spectrometry (AMS) $^{14}C$ measurement (about 200 $\mu$mol), $^{13}C$ measurement (about 100 $\mu$mol), and archive (about 200 $\mu$mol). Efficiency of the $CO_2$ stripping from seawater sample was more than 95 % that was calculated from concentration of DIC in the seawater samples. The stripped $CO_2$ gas for $^{14}C$ was then converted to graphite catalytically on iron powder with pure hydrogen gas. Yield of graphite powder from $CO_2$ gas was estimated to be 73 $\pm$ 9 % in average by weighing of sample graphite powder. Details of these preparation procedures were described by Kumamoto et al. (2000).

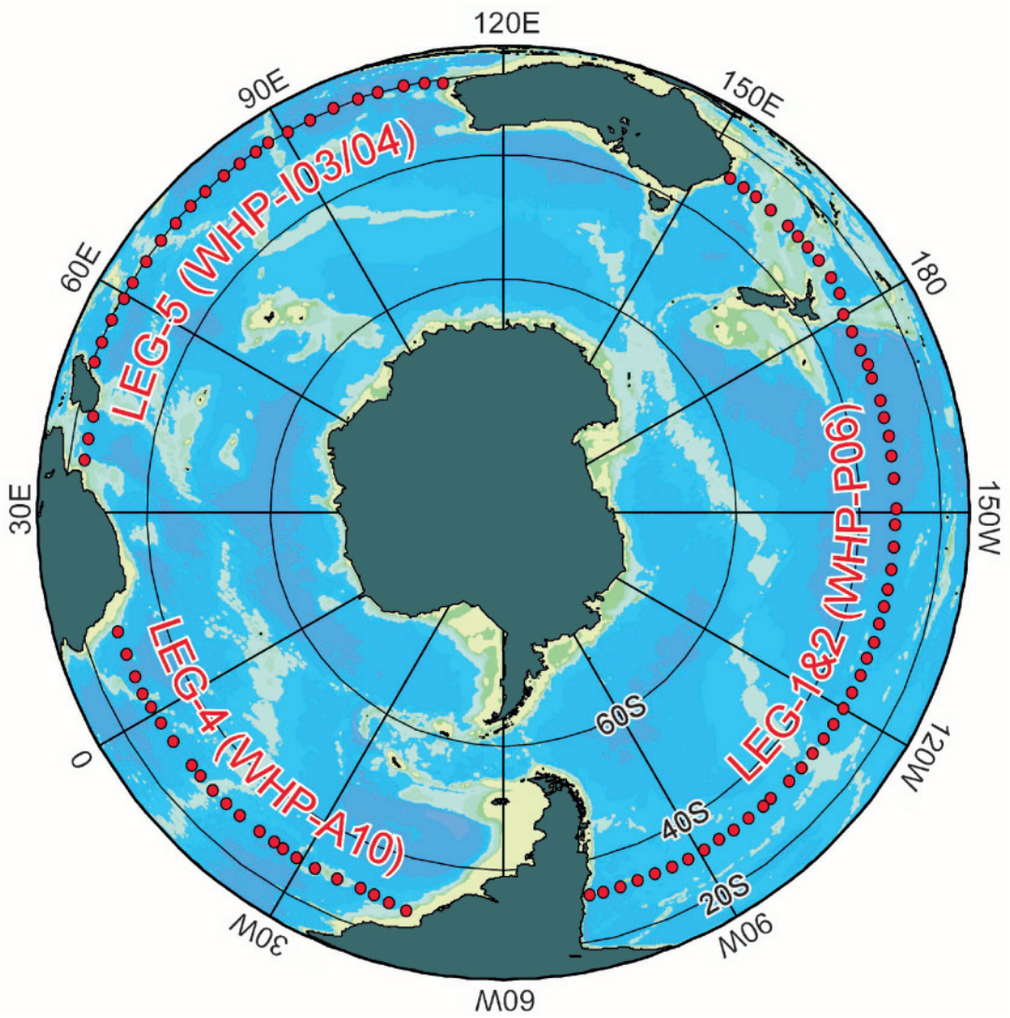


Figure 3.10.1. Sampling stations for $\delta^{13}C$ and $\Delta^{14}C$ of dissolved inorganic carbon during BEAGLE2003 Leg-1 (August-September, 2003), Leg-2 (September-October, 2003), Leg-4 (November-December, 2003), and Leg-5 (December, 2003-January, 2004).

Table 3.10.1. The sampling dates, locations, number of samples, and maximum sampling pressure for carbon isotopes in DIC during BEAGLE2003 Leg-1.

| Station | Date (UTC) | Latitude | Longitude | Number of samples | Number of replicates | Max. pressure /db |
|---|---|---|---|---|---|---|
| P06W-239 | 04/Aug/2003 | 30.087 S | 154.165 E | 31 | 3 | 4,680 |
| P06W-234 | 05/Aug/2003 | 30.081 S | 156.533 E | 32 | 3 | 4,898 |
| P06W-227 | 06/Aug/2003 | 30.079 S | 158.682 E | 24 | 3 | 3,235 |
| P06W-221 | 07/Aug/2003 | 30.086 S | 161.500 E | 15 | 1 | 1,185 |
| P06W-215 | 08/Aug/2003 | 30.086 S | 164.834 E | 26 | 2 | 3,419 |
| P06W-211 | 10/Aug/2003 | 30.084 S | 166.999 E | 23 | 2 | 2,873 |
| P06W-207 | 11/Aug/2003 | 30.084 S | 168.999 E | 25 | 3 | 3,153 |
| P06W-201 | 12/Aug/2003 | 30.089 S | 171.501 E | 20 | 2 | 2,264 |
| P06W-195 | 13/Aug/2003 | 30.083 S | 174.497 E | 27 | 3 | 3,689 |
| P06W-191 | 14/Aug/2003 | 30.582 S | 177.000 E | 30 | 3 | 4,353 |
| P06C-182 | 15/Aug/2003 | 32.501 S | 179.917 E | 24 | 3 | 2,872 |
| P06C-174 | 18/Aug/2003 | 32.502 S | 177.251 W | 36 | 3 | 6,503 |
| P06C-168 | 20/Aug/2003 | 32.497 S | 174.330 W | 36 | 3 | 5,958 |
| P06C-162 | 21/Aug/2003 | 32.500 S | 171.909 W | 29 | 3 | 4,200 |
| P06C-X15 | 22/Aug/2003 | 32.504 S | 170.001 W | 34 | 3 | 5,610 |
| P06C-150 | 24/Aug/2003 | 32.497 S | 166.500 W | 33 | 3 | 5,357 |
| P06C-146 | 26/Aug/2003 | 32.491 S | 163.832 W | 34 | 3 | 5,630 |
| P06C-142 | 27/Aug/2003 | 32.500 S | 161.164 W | 33 | 3 | 5,221 |
| P06C-137 | 28/Aug/2003 | 32.500 S | 158.166 W | 35 | 3 | 5,781 |
| P06C-133 | 29/Aug/2003 | 32.504 S | 154.847 W | 32 | 3 | 5,076 |
| P06C-X16 | 31/Aug/2003 | 32.499 S | 150.499 W | 33 | 3 | 5,234 |
| P06C-125 | 01/Sep/2003 | 32.501 S | 148.160 W | 30 | 3 | 4,626 |
| P06C-121 | 02/Sep/2003 | 32.508 S | 144.831 W | 33 | 3 | 5,354 |
| Total | | | | 675 | 64 | |

Table 3.10.2. As same as Table 3.10.1 but for Leg-2.

| Station | Date (UTC) | Latitude | Longitude | Number of samples | Number of replicates | Max. pressure /db |
|---|---|---|---|---|---|---|
| P06C-117 | 14/Sep/2003 | 32.497 S | 141.494 W | 31 | 3 | 4,762 |
| P06C-113 | 15/Sep/2003 | 32.501 S | 138.665 W | 31 | 3 | 4,640 |
| P06C-109 | 16/Sep/2003 | 32.499 S | 136.003 W | 31 | 3 | 4,456 |
| P06C-105 | 17/Sep/2003 | 32.502 S | 133.344 W | 29 | 3 | 4,306 |
| P06C-101 | 18/Sep/2003 | 32.494 S | 130.660 W | 27 | 3 | 3,650 |
| P06C-097 | 19/Sep/2003 | 32.494 S | 127.997 W | 28 | 3 | 3,988 |
| P06C-093 | 21/Sep/2003 | 32.509 S | 125.336 W | 20 | 2 | 2,183 |
| P06C-089 | 21/Sep/2003 | 32.492 S | 122.658 W | 22 | 2 | 2,625 |
| P06C-085 | 22/Sep/2003 | 32.501 S | 119.992 W | 24 | 3 | 3,089 |
| P06C-081 | 23/Sep/2003 | 32.499 S | 117.320 W | 26 | 3 | 3,352 |
| P06C-077 | 24/Sep/2003 | 32.500 S | 114.668 W | 24 | 2 | 2,970 |
| P06E-071 | 25/Sep/2003 | 32.499 S | 111.999 W | 23 | 2 | 2,722 |
| P06E-067 | 26/Sep/2003 | 32.500 S | 109.343 W | 30 | 3 | 4,496 |
| P06E-063 | 27/Sep/2003 | 32.501 S | 106.674 W | 26 | 3 | 3,343 |
| P06E-X18 | 28/Sep/2003 | 32.500 S | 103.000 W | 27 | 3 | 3,617 |
| P06E-055 | 29/Sep/2003 | 32.503 S | 101.332 W | 27 | 3 | 3,622 |
| P06E-051 | 01/Oct/2003 | 32.501 S | 98.667 W | 28 | 3 | 3,847 |
| P06E-047 | 02/Oct/2003 | 32.498 S | 96.000 W | 28 | 3 | 4,012 |
| P06E-043 | 02/Oct/2003 | 32.501 S | 93.338 W | 23 | 2 | 2,691 |
| P06E-039 | 03/Oct/2003 | 32.500 S | 90.682 W | 27 | 3 | 3,741 |
| P06E-X19 | 04/Oct/2003 | 32.503 S | 87.994 W | 27 | 3 | 3,774 |
| P06E-031 | 05/Oct/2003 | 32.497 S | 85.334 W | 28 | 3 | 4,054 |
| P06E-027 | 06/Oct/2003 | 32.501 S | 82.664 W | 28 | 3 | 3,934 |
| P06E-023 | 08/Oct/2003 | 32.502 S | 79.997 W | 23 | 2 | 2,811 |
| P06E-019 | 09/Oct/2003 | 32.495 S | 77.328 W | 26 | 3 | 3,608 |
| P06E-015 | 10/Oct/2003 | 32.497 S | 74.673 W | 28 | 3 | 3,886 |
| P06E-011 | 11/Oct/2003 | 32.495 S | 72.716 W | 36 | 3 | 6,054 |
| Total | | | | 728 | 75 | |

Table 3.10.3. As same as Table 3.10.1 but for Leg-4.

| Station | Date (UTC) | Latitude | Longitude | Number of samples | Number of replicates | Max. pressure /db |
|---|---|---|---|---|---|---|
| A10-629 | 08/Nov/2003 | 28.044 S | 46.127 W | 22 | 2 | 2,429 |
| A10-003 | 09/Nov/2003 | 28.832 S | 43.593 W | 28 | 3 | 3,935 |
| A10-007 | 10/Nov/2003 | 29.613 S | 41.161 W | 28 | 3 | 3,835 |
| A10-X17 | 11/Nov/2003 | 30.098 S | 39.037 W | 30 | 2 | 4,249 |
| A10-021 | 12/Nov/2003 | 30.001 S | 35.488 W | 22 | 1 | 2,328 |
| A10-029 | 14/Nov/2003 | 30.000 S | 32.007 W | 28 | 2 | 3,862 |
| A10-035 | 16/Nov/2003 | 29.998 S | 29.003 W | 26 | 2 | 3,199 |
| A10-038 | 17/Nov/2003 | 29.999 S | 26.716 W | 35 | 2 | 5,368 |
| A10-X16 | 17/Nov/2003 | 30.220 S | 25.049 W | 31 | 2 | 4,411 |
| A10-043 | 18/Nov/2003 | 30.000 S | 22.482 W | 32 | 2 | 4,660 |
| A10-X15 | 19/Nov/2003 | 30.109 S | 19.007 W | 31 | 2 | 4,671 |
| A10-051 | 20/Nov/2003 | 30.002 S | 16.334 W | 28 | 2 | 3,741 |
| A10-055 | 21/Nov/2003 | 30.003 S | 13.665 W | 22 | 2 | 2,317 |
| A10-059 | 22/Nov/2003 | 30.000 S | 11.001 W | 28 | 2 | 3,767 |
| A10-X14 | 22/Nov/2003 | 30.003 S | 8.999 W | 29 | 2 | 3,981 |
| A10-067 | 24/Nov/2003 | 30.000 S | 4.829 W | 31 | 2 | 4,302 |
| A10-071 | 26/Nov/2003 | 30.001 S | 1.505 W | 32 | 2 | 4,789 |
| A10-075 | 27/Nov/2003 | 29.732 S | 1.122 E | 28 | 2 | 3,747 |
| A10-079 | 27/Nov/2003 | 29.467 S | 3.302 E | 32 | 2 | 4,816 |
| A10-083 | 29/Nov/2003 | 29.746 S | 5.931 E | 34 | 2 | 5,204 |
| A10-087 | 30/Nov/2003 | 29.745 S | 9.288 E | 34 | 2 | 5,067 |
| A10-093 | 01/Dec/2003 | 29.372 S | 12.790 E | 28 | 3 | 3,250 |
| Total | | | | 639 | 46 | |

Table 3.10.4. As same as Table 3.10.1 but for Leg-5.

| Station | Date (UTC) | Latitude | Longitude | Number of samples | Number of replicates | Max. pressure /db |
|---|---|---|---|---|---|---|
| I04-601 | 14/Dec/2003 | 24.673 S | 36.991 E | 25 | 2 | 3,084 |
| I04-595 | 15/Dec/2003 | 24.661 S | 39.996 E | 27 | 2 | 3,578 |
| I04-589 | 16/Dec/2003 | 24.665 S | 42.997 E | 28 | 2 | 3,725 |
| I03-557 | 21/Dec/2003 | 19.997 S | 50.060 E | 31 | 2 | 4,401 |
| I03-551 | 22/Dec/2003 | 19.985 S | 52.777 E | 34 | 1 | 5,002 |
| I03-545 | 23/Dec/2003 | 19.999 S | 56.092 E | 31 | 2 | 4,441 |
| I03-535 | 25/Dec/2003 | 20.380 S | 59.228 E | 33 | 2 | 4,823 |
| I03-531 | 28/Dec/2003 | 20.368 S | 61.631 E | 28 | 2 | 3,650 |
| I03-525 | 29/Dec/2003 | 20.089 S | 64.934 E | 27 | 1 | 2,935 |
| I03-519 | 30/Dec/2003 | 19.998 S | 68.213 E | 23 | 1 | 2,541 |
| I03-513 | 01/Jan/2004 | 19.997 S | 71.256 E | 30 | 1 | 4,240 |
| I03-507 | 02/Jan/2004 | 20.000 S | 74.167 E | 33 | 2 | 5,032 |
| I03-503 | 03/Jan/2004 | 19.987 S | 76.908 E | 34 | 2 | 5,168 |
| I03-X08 | 05/Jan/2004 | 19.996 S | 79.998 E | 34 | 2 | 4,928 |
| I03-495 | 06/Jan/2004 | 19.996 S | 82.736 E | 34 | 2 | 5,305 |
| I03-491 | 07/Jan/2004 | 19.990 S | 85.304 E | 33 | 2 | 4,951 |
| I03-487 | 09/Jan/2004 | 20.000 S | 87.333 E | 20 | 1 | 2,022 |
| I03-480 | 10/Jan/2004 | 19.992 S | 90.288 E | 35 | 2 | 5,251 |
| I03-474 | 11/Jan/2004 | 19.991 S | 93.533 E | 35 | 2 | 5,410 |
| I03-470 | 13/Jan/2004 | 19.991 S | 96.953 E | 35 | 2 | 5,419 |
| I03-466 | 14/Jan/2004 | 19.990 S | 100.466 E | 36 | 2 | 6,067 |
| I03-463 | 16/Jan/2004 | 19.992 S | 103.129 E | 36 | 2 | 5,751 |
| I03-459 | 17/Jan/2004 | 19.996 S | 106.625 E | 36 | 3 | 5,617 |
| I03-455 | 18/Jan/2004 | 20.932 S | 109.445 E | 34 | 3 | 5,140 |
| I03-451 | 20/Jan/2004 | 21.825 S | 111.902 E | 33 | 3 | 5,019 |
| Total | | | | 785 | 48 | |

**(5) Sample measurements**

$\delta^{13}C$ of the sample $CO_2$ gas was measured using Finnigan MAT252 mass spectrometer. The $\delta^{13}C$ value was calculated by a following equation:

$$\delta^{13}C\ (‰) = (R_{sample} / R_{standard} - 1) \times 1000, \quad (1)$$

where $R_{sample}$ and $R_{standard}$ denote $^{13}C$ / $^{12}C$ ratios of the sample $CO_2$ gas and the standard $CO_2$ gas, respectively. The working standard gas was purchased from Oztech Gas Co. with assigned $\delta^{13}C$ value of –3.64 ‰ versus VPDB (Lot No. SHO-873C). The gas has been calibrated relative to the appropriate internationally accepted IAEA primary standards. $\Delta^{14}C$ in the graphite sample was measured in AMS facilities of Institute of Accelerator Analysis Ltd in Shirakawa (Pelletron 9SDH-2, NEC) and Paleo Labo Co. Ltd in Kiryu (Compact-AMS, NEC), Japan. The $\Delta^{14}C$ value was calculated by:

$$\delta^{14}C\ (‰) = (R_{sample} / R_{standard} - 1) \times 1000, \quad (2)$$

$$\Delta^{14}C\ (‰) = \delta^{14}C - 2\ (\delta^{13}C + 25)\ (1 + \delta^{14}C / 1000), \quad (3)$$

where $R_{sample}$ and $R_{standard}$ denote, respectively, $^{14}C$ / $^{12}C$ ratios of the sample and the international standard, NIST Oxalic Acid SRM4990-C (HOxII). $R_{standard}$ was corrected for decay since A.D. 1950 (Stuiver and Polach, 1977; Stuiver, 1983). Equation 3 is normalization for isotopic fractionation. When quality of $\delta^{13}C$ data was not "good", $\Delta^{14}C$ was calculated by interpolated $\delta^{13}C$ value derived from data at just above and below layers. Finally $\Delta^{14}C$ value was corrected for radiocarbon decay between the sampling and the measurement dates. Individual errors of $\delta^{13}C$ were given by standard deviation of repeat measurements. Errors of $\Delta^{14}C$ were derived from larger of the standard deviation of repeat measurements and the counting error. Means of the $\delta^{13}C$ and $\Delta^{14}C$ errors were calculated to be 0.004 ‰ and 3.6 ‰ that probably correspond to "repeatabilities" of our $\delta^{13}C$ and $\Delta^{14}C$ measurements. It should be noted that these errors did not include error due to sample preparation.

**(6) Replicate measurements**

Replicate samples were taken at all the 97 stations. Results of 233 pairs of the replicate samples are shown in Table 3.10.5. The standard deviations of the $\delta^{13}C$ and $\Delta^{14}C$ replicate analyses were calculated to be 0.020 ‰ (n = 217) and 3.9 ‰ (n = 214), respectively. The standard deviations of $\delta^{13}C$ replicate analyses during Leg-1, Leg-2, Leg-4, and Leg-5 were 0.021 (n = 58), 0.019 (n = 74), 0.020 (n = 42), and 0.019 ‰ (n = 43), respectively. The standard deviation of $\Delta^{14}C$ replicate analyses during Leg-1, Leg-2, Leg-4, and Leg-5 were 3.6 (n = 62), 3.7 (n = 68), 4.4 (n = 37), and 3.9 ‰ (n = 47), respectively.

Table 3.10.5. Summary of replicate analyses.

| Station | Btl | $\delta^{13}C$ / ‰ | | | | $\Delta^{14}C$ / ‰ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ | Error[a] | E.W.Mean[b] | Uncertainty[c] | $\Delta^{14}C$ | Error[d] | E.W.Mean[b] | Uncertainty[c] |
| P06W-239 | 32 | 0.949 | 0.002 | 0.930 | 0.028 | 79.5 | 3.8 | 78.0 | 3.0 |
| | | 0.910 | 0.002 | | | 75.7 | 4.8 | | |
| P06W-239 | 21 | 0.484 | 0.003 | 0.483 | 0.003 | –170.4 | 3.3 | –171.0 | 2.3 |
| | | 0.482 | 0.003 | | | –171.4 | 3.1 | | |
| P06W-239 | 13 | 0.437 | 0.005 | 0.408 | 0.028 | –165.5 | 3.2 | –167.7 | 3.0 |
| | | 0.397 | 0.003 | | | –169.8 | 3.2 | | |
| P06W-234 | 32 | 1.135 | 0.004 | 1.124 | 0.012 | 83.6 | 3.8 | 81.9 | 2.7 |
| | | 1.118 | 0.003 | | | 80.1 | 3.8 | | |
| P06W-234 | 21 | 0.608 | 0.003 | 0.615 | 0.009 | –147.3 | 3.2 | –146.1 | 2.3 |
| | | 0.621 | 0.003 | | | –144.9 | 3.2 | | |
| P06W-234 | 13 | 0.385 | 0.004 | 0.471 | 0.064 | –155.8 | 4.4 | –159.2 | 4.7 |
| | | 0.476 | 0.001 | | | –162.5 | 4.4 | | |
| P06W-227 | 32 | 0.918 | 0.002 | 0.914 | 0.006 | 92.8 | 5.4 | 91.1 | 3.7 |
| | | 0.910 | 0.002 | | | 89.5 | 5.2 | | |
| P06W-227 | 21 | 0.542 | 0.002 | 0.540 | 0.007 | –166.9 | 4.4 | –165.6 | 3.1 |
| | | 0.532 | 0.004 | | | –164.2 | 4.4 | | |
| P06W-227 | 13 | 0.440 | 0.003 | 0.394 | 0.036 | –165.9 | 4.4 | –164.9 | 3.1 |
| | | 0.389 | 0.001 | | | –163.9 | 4.4 | | |
| P06W-221 | 32 | 0.956 | 0.004 | 0.941 | 0.022 | - | - | - | - |
| | | 0.925 | 0.004 | | | - | - | | |
| P06W-215 | 32 | 0.979 | 0.003 | 0.963 | 0.023 | - | - | - | - |
| | | 0.947 | 0.003 | | | - | - | | |
| P06W-215 | 21 | 0.530 | 0.002 | 0.531 | 0.002 | –142.7 | 4.2 | –140.1 | 3.7 |
| | | 0.533 | 0.003 | | | –137.4 | 4.3 | | |
| P06W-211 | 32 | 0.994 | 0.002 | 0.975 | 0.043 | 88.6 | 4.0 | 91.1 | 3.5 |
| | | 0.933 | 0.003 | | | 93.6 | 4.0 | | |
| P06W-211 | 21 | 0.546 | 0.006 | 0.542 | 0.004 | –158.5 | 3.3 | –161.4 | 3.7 |
| | | 0.541 | 0.003 | | | –163.7 | 2.9 | | |
| P06W-207 | 32 | 1.086 | 0.003 | 1.091 | 0.005 | 85.3 | 4.0 | 83.2 | 3.1 |
| | | 1.093 | 0.002 | | | 80.9 | 4.1 | | |

Table 3.10.5. continued.

| Station | Btl | $\delta^{13}C$ / ‰ | | | | $\Delta^{14}C$ / ‰ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ | Error[a] | E.W.Mean[b] | Uncertainty[c] | $\Delta^{14}C$ | Error[d] | E.W.Mean[b] | Uncertainty[c] |
| P06W-207 | 21 | 0.615 | 0.005 | 0.594 | 0.025 | –148.3 | 3.4 | –153.7 | 7.6 |
| | | 0.580 | 0.004 | | | –159.1 | 3.4 | | |
| P06W-207 | 13 | 0.197 | 0.003 | 0.182 | 0.022 | –208.4 | 3.1 | –207.4 | 2.2 |
| | | 0.166 | 0.003 | | | –206.3 | 3.1 | | |
| P06W-201 | 32 | - | - | - | - | 80.7 | 3.8 | 80.8 | 2.7 |
| | | - | - | | | 80.9 | 3.7 | | |
| P06W-201 | 21 | 0.548 | 0.002 | 0.579 | 0.044 | –149.4 | 3.3 | –151.6 | 4.5 |
| | | 0.610 | 0.002 | | | –155.8 | 4.5 | | |
| P06W-195 | 32 | 0.984 | 0.002 | 0.985 | 0.005 | 86.9 | 6.1 | 89.9 | 3.1 |
| | | 0.991 | 0.005 | | | 90.9 | 3.6 | | |
| P06W-195 | 21 | 0.533 | 0.003 | 0.547 | 0.020 | –163.2 | 3.2 | –163.1 | 2.3 |
| | | 0.561 | 0.003 | | | –162.9 | 3.2 | | |
| P06W-195 | 13 | - | - | - | - | –202.6 | 3.1 | –206.8 | 5.9 |
| | | - | - | | | –211.0 | 3.1 | | |
| P06W-191 | 32 | 0.987 | 0.004 | 0.988 | 0.002 | 77.3 | 3.7 | 74.6 | 4.0 |
| | | 0.988 | 0.003 | | | 71.7 | 3.8 | | |
| P06W-191 | 21 | 0.540 | 0.002 | 0.539 | 0.003 | –173.5 | 3.1 | –171.9 | 2.3 |
| | | 0.536 | 0.004 | | | –170.3 | 3.1 | | |
| P06W-191 | 13 | 0.190 | 0.003 | 0.173 | 0.017 | –209.3 | 3.0 | –212.1 | 4.2 |
| | | 0.166 | 0.002 | | | –215.2 | 3.2 | | |
| P06C-182 | 32 | 1.039 | 0.004 | 1.033 | 0.009 | 73.3 | 4.0 | 71.9 | 3.1 |
| | | 1.026 | 0.004 | | | 69.5 | 5.0 | | |
| P06C-182 | 21 | 0.653 | 0.005 | 0.645 | 0.013 | –143.8 | 3.4 | –148.5 | 6.2 |
| | | 0.634 | 0.006 | | | –152.5 | 3.1 | | |
| P06C-182 | 13 | 0.294 | 0.003 | 0.297 | 0.006 | –197.8 | 3.2 | –201.3 | 4.8 |
| | | 0.303 | 0.004 | | | –204.6 | 3.1 | | |
| P06C-174 | 32 | 1.043 | 0.002 | 1.047 | 0.009 | 73.4 | 4.2 | 74.6 | 3.0 |
| | | 1.056 | 0.003 | | | 75.7 | 4.3 | | |
| P06C-174 | 21 | 0.664 | 0.005 | 0.657 | 0.006 | –147.0 | 3.4 | –150.9 | 5.4 |
| | | 0.656 | 0.002 | | | –154.6 | 3.3 | | |

Table 3.10.5. continued.

| Station | Btl | $\delta^{13}C$ / ‰ | | | | $\Delta^{14}C$ / ‰ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ | Error[a] | E.W.Mean[b] | Uncertainty[c] | $\Delta^{14}C$ | Error[d] | E.W.Mean[b] | Uncertainty[c] |
| P06C-174 | 13 | - | - | - | - | –177.3 | 3.1 | –180.1 | 4.3 |
| | | - | - | | | –183.4 | 3.4 | | |
| P06C-168 | 32 | 1.067 | 0.002 | 1.070 | 0.013 | 75.1 | 4.5 | 75.4 | 3.0 |
| | | 1.086 | 0.005 | | | 75.6 | 4.1 | | |
| P06C-168 | 21 | 0.619 | 0.004 | 0.636 | 0.015 | –150.4 | 3.4 | –153.2 | 4.1 |
| | | 0.640 | 0.002 | | | –156.2 | 3.5 | | |
| P06C-168 | 13 | 0.202 | 0.005 | 0.215 | 0.013 | –219.0 | 3.1 | –218.7 | 2.3 |
| | | 0.220 | 0.003 | | | –218.3 | 3.3 | | |
| P06C-162 | 32 | 1.077 | 0.005 | 1.077 | 0.002 | 71.6 | 4.5 | 73.4 | 3.1 |
| | | 1.077 | 0.002 | | | 75.0 | 4.4 | | |
| P06C-162 | 21 | 0.639 | 0.002 | 0.636 | 0.018 | –143.0 | 3.6 | –144.7 | 2.6 |
| | | 0.614 | 0.005 | | | –146.6 | 3.7 | | |
| P06C-162 | 13 | 0.255 | 0.005 | 0.263 | 0.008 | –204.1 | 3.4 | –207.2 | 4.4 |
| | | 0.266 | 0.003 | | | –210.3 | 3.4 | | |
| P06C-X15 | 32 | 1.106 | 0.003 | 1.098 | 0.021 | 69.7 | 3.7 | 69.1 | 2.7 |
| | | 1.077 | 0.005 | | | 68.4 | 4.0 | | |
| P06C-X15 | 21 | 0.595 | 0.003 | 0.615 | 0.021 | –146.2 | 3.2 | –152.2 | 8.8 |
| | | 0.624 | 0.002 | | | –158.7 | 3.3 | | |
| P06C-X15 | 13 | 0.228 | 0.004 | 0.226 | 0.001 | –210.4 | 3.1 | –208.4 | 3.0 |
| | | 0.226 | 0.001 | | | –206.2 | 3.2 | | |
| P06C-150 | 32 | 1.138 | 0.004 | 1.126 | 0.017 | 78.6 | 3.8 | 77.1 | 2.7 |
| | | 1.114 | 0.004 | | | 75.5 | 3.7 | | |
| P06C-150 | 21 | 0.659 | 0.005 | 0.657 | 0.004 | –151.7 | 3.4 | –148.8 | 4.0 |
| | | 0.654 | 0.005 | | | –146.1 | 3.3 | | |
| P06C-150 | 13 | 0.212 | 0.001 | 0.210 | 0.011 | –214.2 | 3.2 | –214.9 | 2.2 |
| | | 0.196 | 0.003 | | | –215.5 | 3.1 | | |
| P06C-146 | 32 | 1.178 | 0.004 | 1.152 | 0.037 | 81.2 | 4.2 | 80.4 | 2.9 |
| | | 1.126 | 0.004 | | | 79.6 | 4.1 | | |
| P06C-146 | 21 | - | - | - | - | –142.7 | 3.5 | –143.5 | 2.5 |
| | | - | - | | | –144.3 | 3.5 | | |

Table 3.10.5. continued.

| Station | Btl | $\delta^{13}C$ / ‰ | | | | $\Delta^{14}C$ / ‰ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ | Error[a] | E.W.Mean[b] | Uncertainty[c] | $\Delta^{14}C$ | Error[d] | E.W.Mean[b] | Uncertainty[c] |
| P06C-146 | 13 | 0.168 | 0.004 | 0.191 | 0.033 | –222.9 | 3.3 | –220.6 | 3.4 |
| | | 0.214 | 0.004 | | | –218.1 | 3.4 | | |
| P06C-142 | 32 | 1.163 | 0.003 | 1.151 | 0.018 | 76.4 | 3.8 | 71.3 | 7.7 |
| | | 1.138 | 0.003 | | | 65.5 | 4.1 | | |
| P06C-142 | 21 | 0.671 | 0.004 | 0.654 | 0.015 | –144.7 | 3.4 | –142.4 | 3.2 |
| | | 0.650 | 0.002 | | | –140.2 | 3.4 | | |
| P06C-142 | 13 | 0.182 | 0.005 | 0.185 | 0.005 | –212.2 | 2.9 | –213.3 | 2.1 |
| | | 0.189 | 0.006 | | | –214.7 | 3.1 | | |
| P06C-137 | 32 | 1.131 | 0.003 | 1.120 | 0.029 | 84.7 | 3.6 | 82.9 | 2.5 |
| | | 1.090 | 0.005 | | | 81.2 | 3.5 | | |
| P06C-137 | 21 | 0.597 | 0.003 | 0.600 | 0.005 | –145.7 | 3.0 | –142.0 | 5.2 |
| | | 0.604 | 0.004 | | | –138.3 | 3.0 | | |
| P06C-137 | 13 | 0.210 | 0.003 | 0.227 | 0.023 | –209.3 | 3.0 | –213.1 | 5.6 |
| | | 0.243 | 0.003 | | | –217.2 | 3.1 | | |
| P06C-133 | 32 | - | - | - | - | 86.7 | 4.3 | 89.8 | 4.3 |
| | | - | - | | | 92.8 | 4.2 | | |
| P06C-133 | 21 | 0.639 | 0.004 | 0.615 | 0.034 | –146.7 | 3.6 | –144.9 | 2.5 |
| | | 0.591 | 0.004 | | | –143.1 | 3.6 | | |
| P06C-133 | 13 | 0.232 | 0.002 | 0.234 | 0.008 | –214.9 | 3.5 | –212.7 | 3.0 |
| | | 0.244 | 0.005 | | | –210.7 | 3.4 | | |
| P06C-X16 | 32 | 1.230 | 0.004 | 1.222 | 0.008 | 99.8 | 3.7 | 100.9 | 2.7 |
| | | 1.218 | 0.003 | | | 102.0 | 3.8 | | |
| P06C-X16 | 21 | 0.573 | 0.004 | 0.596 | 0.032 | –145.1 | 3.2 | –147.7 | 3.6 |
| | | 0.618 | 0.004 | | | –150.2 | 3.2 | | |
| P06C-X16 | 13 | 0.198 | 0.003 | 0.228 | 0.031 | –210.8 | 3.2 | –211.8 | 2.2 |
| | | 0.242 | 0.002 | | | –212.7 | 3.0 | | |
| P06C-125 | 32 | 1.282 | 0.002 | 1.278 | 0.006 | 83.6 | 3.8 | 83.0 | 2.7 |
| | | 1.274 | 0.002 | | | 82.5 | 3.7 | | |
| P06C-125 | 21 | 0.607 | 0.004 | 0.619 | 0.009 | –155.4 | 3.1 | –158.9 | 5.4 |
| | | 0.620 | 0.001 | | | –163.0 | 3.3 | | |

Table 3.10.5. continued.

| Station | Btl | $\delta^{13}C$ / ‰ | | | | $\Delta^{14}C$ / ‰ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ | Error[a] | E.W.Mean[b] | Uncertainty[c] | $\Delta^{14}C$ | Error[d] | E.W.Mean[b] | Uncertainty[c] |
| P06C-125 | 13 | 0.245 | 0.007 | 0.263 | 0.017 | –214.7 | 3.0 | –212.5 | 3.0 |
| | | 0.269 | 0.004 | | | –210.5 | 2.9 | | |
| P06C-121 | 32 | - | - | - | - | 79.9 | 3.8 | 80.3 | 2.7 |
| | | - | - | | | 80.7 | 3.8 | | |
| P06C-121 | 21 | 0.571 | 0.003 | 0.587 | 0.016 | –154.9 | 4.2 | –151.0 | 4.4 |
| | | 0.594 | 0.002 | | | –148.7 | 3.2 | | |
| P06C-121 | 13 | 0.258 | 0.002 | 0.262 | 0.013 | –211.2 | 3.0 | –208.9 | 3.4 |
| | | 0.277 | 0.004 | | | –206.4 | 3.1 | | |
| P06C-117 | 32 | 1.236 | 0.004 | 1.249 | 0.023 | - | - | - | - |
| | | 1.269 | 0.005 | | | - | - | | |
| P06C-117 | 21 | 0.592 | 0.003 | 0.571 | 0.021 | –148.1 | 3.3 | –153.5 | 7.6 |
| | | 0.562 | 0.002 | | | –158.8 | 3.3 | | |
| P06C-117 | 13 | 0.261 | 0.005 | 0.260 | 0.003 | –205.8 | 3.0 | –206.9 | 2.1 |
| | | 0.260 | 0.003 | | | –207.8 | 2.9 | | |
| P06C-113 | 32 | 1.257 | 0.004 | 1.221 | 0.040 | 92.5 | 3.7 | 91.6 | 2.6 |
| | | 1.201 | 0.003 | | | 90.6 | 3.7 | | |
| P06C-113 | 21 | 0.585 | 0.005 | 0.630 | 0.033 | –145.1 | 3.2 | –145.6 | 2.3 |
| | | 0.632 | 0.001 | | | –146.2 | 3.3 | | |
| P06C-113 | 13 | 0.262 | 0.002 | 0.266 | 0.013 | –213.1 | 3.0 | –210.3 | 4.2 |
| | | 0.280 | 0.004 | | | –207.2 | 3.2 | | |
| P06C-109 | 32 | 1.323 | 0.004 | 1.276 | 0.052 | 91.1 | 3.8 | 86.1 | 7.4 |
| | | 1.250 | 0.003 | | | 80.7 | 4.0 | | |
| P06C-109 | 21 | 0.532 | 0.003 | 0.542 | 0.013 | –160.6 | 3.4 | –156.2 | 6.2 |
| | | 0.551 | 0.003 | | | –151.9 | 3.4 | | |
| P06C-109 | 13 | 0.293 | 0.002 | 0.295 | 0.004 | –213.6 | 3.2 | –213.9 | 2.3 |
| | | 0.299 | 0.003 | | | –214.2 | 3.3 | | |
| P06C-105 | 32 | 1.359 | 0.002 | 1.348 | 0.025 | 88.4 | 3.9 | 84.6 | 5.4 |
| | | 1.323 | 0.003 | | | 80.7 | 4.0 | | |
| P06C-105 | 21 | 0.552 | 0.005 | 0.569 | 0.016 | –158.2 | 3.3 | –157.0 | 2.3 |
| | | 0.575 | 0.003 | | | –156.0 | 3.2 | | |

Table 3.10.5. continued.

| Station | Btl | $\delta^{13}C$ / ‰ | | | | $\Delta^{14}C$ / ‰ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ | Error[a] | E.W.Mean[b] | Uncertainty[c] | $\Delta^{14}C$ | Error[d] | E.W.Mean[b] | Uncertainty[c] |
| P06C-105 | 13 | 0.276 | 0.005 | 0.328 | 0.038 | –208.5 | 3.1 | –210.8 | 3.3 |
| | | 0.330 | 0.001 | | | –213.2 | 3.1 | | |
| P06C-101 | 32 | 1.231 | 0.004 | 1.244 | 0.014 | 95.0 | 3.8 | 92.5 | 6.6 |
| | | 1.251 | 0.003 | | | 85.7 | 6.3 | | |
| P06C-101 | 21 | 0.555 | 0.006 | 0.562 | 0.005 | –145.8 | 3.2 | –147.4 | 2.3 |
| | | 0.562 | 0.001 | | | –149.0 | 3.2 | | |
| P06C-101 | 13 | 0.297 | 0.005 | 0.259 | 0.044 | –208.6 | 2.9 | –207.3 | 2.1 |
| | | 0.235 | 0.004 | | | –206.0 | 3.0 | | |
| P06C-097 | 32 | - | - | - | - | 100.4 | 3.8 | 105.7 | 7.6 |
| | | - | - | | | 111.2 | 3.9 | | |
| P06C-097 | 21 | 0.617 | 0.005 | 0.577 | 0.033 | –138.7 | 3.1 | –138.8 | 2.2 |
| | | 0.571 | 0.002 | | | –138.8 | 3.0 | | |
| P06C-097 | 13 | 0.303 | 0.003 | 0.297 | 0.009 | –198.7 | 2.9 | –201.7 | 4.0 |
| | | 0.290 | 0.003 | | | –204.4 | 2.8 | | |
| P06C-093 | 32 | 1.208 | 0.001 | 1.209 | 0.007 | 83.7 | 3.6 | 87.5 | 5.4 |
| | | 1.218 | 0.003 | | | 91.4 | 3.7 | | |
| P06C-093 | 21 | 0.515 | 0.004 | 0.517 | 0.002 | –155.6 | 3.1 | –156.8 | 2.2 |
| | | 0.518 | 0.003 | | | –157.8 | 3.0 | | |
| P06C-089 | 32 | 1.267 | 0.007 | 1.251 | 0.013 | 90.6 | 3.7 | 89.5 | 2.6 |
| | | 1.248 | 0.003 | | | 88.4 | 3.7 | | |
| P06C-089 | 21 | 0.578 | 0.003 | 0.562 | 0.042 | –157.9 | 3.1 | –156.8 | 2.2 |
| | | 0.519 | 0.005 | | | –155.6 | 3.2 | | |
| P06C-085 | 32 | 1.374 | 0.002 | 1.375 | 0.004 | 90.4 | 3.5 | 91.7 | 2.5 |
| | | 1.379 | 0.006 | | | 93.1 | 3.7 | | |
| P06C-085 | 21 | 0.543 | 0.003 | 0.548 | 0.005 | –151.6 | 2.9 | –153.7 | 3.1 |
| | | 0.550 | 0.002 | | | –156.0 | 3.0 | | |
| P06C-085 | 13 | 0.283 | 0.004 | 0.282 | 0.002 | –204.5 | 2.9 | –206.8 | 3.3 |
| | | 0.282 | 0.003 | | | –209.2 | 3.0 | | |
| P06C-081 | 32 | 1.275 | 0.005 | 1.271 | 0.004 | 87.4 | 3.5 | 83.2 | 6.4 |
| | | 1.270 | 0.003 | | | 78.4 | 3.7 | | |

Table 3.10.5. continued.

| Station | Btl | $\delta^{13}C$ / ‰ | | | | $\Delta^{14}C$ / ‰ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ | Error[a] | E.W.Mean[b] | Uncertainty[c] | $\Delta^{14}C$ | Error[d] | E.W.Mean[b] | Uncertainty[c] |
| P06C-081 | 21 | 0.565 | 0.003 | 0.565 | 0.003 | –155.3 | 4.2 | –146.6 | 9.3 |
| | | 0.565 | 0.005 | | | –142.2 | 3.0 | | |
| P06C-081 | 13 | 0.287 | 0.004 | 0.286 | 0.002 | –204.0 | 2.9 | –203.5 | 2.1 |
| | | 0.286 | 0.002 | | | –202.9 | 3.0 | | |
| P06C-077 | 32 | 1.450 | 0.004 | 1.444 | 0.018 | 69.9 | 3.7 | 70.2 | 2.6 |
| | | 1.425 | 0.007 | | | 70.4 | 3.7 | | |
| P06C-077 | 21 | 0.473 | 0.004 | 0.496 | 0.032 | –150.5 | 3.1 | –150.3 | 2.1 |
| | | 0.518 | 0.004 | | | –150.1 | 2.9 | | |
| P06E-071 | 32 | 1.294 | 0.004 | 1.290 | 0.006 | 90.6 | 4.0 | 91.0 | 2.8 |
| | | 1.286 | 0.004 | | | 91.4 | 4.0 | | |
| P06E-071 | 21 | 0.477 | 0.004 | 0.481 | 0.006 | –153.8 | 3.4 | –157.2 | 4.7 |
| | | 0.486 | 0.005 | | | –160.4 | 3.3 | | |
| P06E-067 | 32 | 1.296 | 0.004 | 1.293 | 0.003 | 89.5 | 4.0 | 92.2 | 3.6 |
| | | 1.292 | 0.002 | | | 94.6 | 3.8 | | |
| P06E-067 | 21 | 0.383 | 0.002 | 0.375 | 0.007 | –173.5 | 3.2 | –174.8 | 2.3 |
| | | 0.373 | 0.001 | | | –176.3 | 3.4 | | |
| P06E-067 | 13 | 0.322 | 0.004 | 0.300 | 0.031 | –202.9 | 3.2 | –201.6 | 2.3 |
| | | 0.278 | 0.004 | | | –200.3 | 3.2 | | |
| P06E-063 | 32 | 1.356 | 0.002 | 1.358 | 0.008 | 98.1 | 3.9 | 97.5 | 2.8 |
| | | 1.368 | 0.004 | | | 96.7 | 4.0 | | |
| P06E-063 | 21 | 0.337 | 0.005 | 0.352 | 0.018 | –175.2 | 3.3 | –174.7 | 2.8 |
| | | 0.362 | 0.004 | | | –173.2 | 5.6 | | |
| P06E-063 | 13 | 0.329 | 0.003 | 0.331 | 0.004 | –197.9 | 3.3 | –195.8 | 3.0 |
| | | 0.334 | 0.004 | | | –193.6 | 3.3 | | |
| P06E-X18 | 21 | 0.353 | 0.001 | 0.352 | 0.023 | –182.0 | 3.0 | –179.1 | 4.1 |
| | | 0.320 | 0.005 | | | –176.2 | 3.0 | | |
| P06E-X18 | 13 | 0.314 | 0.002 | 0.319 | 0.018 | –198.1 | 2.9 | –194.6 | 5.2 |
| | | 0.340 | 0.004 | | | –190.7 | 3.0 | | |
| P06E-X18 | 1 | 1.417 | 0.004 | 1.407 | 0.008 | 88.3 | 3.6 | 87.5 | 2.5 |
| | | 1.405 | 0.002 | | | 86.7 | 3.6 | | |

Table 3.10.5. continued.

| Station | Btl | $\delta^{13}C$ / ‰ | | | | $\Delta^{14}C$ / ‰ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ | Error[a] | E.W.Mean[b] | Uncertainty[c] | $\Delta^{14}C$ | Error[d] | E.W.Mean[b] | Uncertainty[c] |
| P06E-055 | 32 | 1.393 | 0.007 | 1.366 | 0.023 | 93.0 | 3.7 | 89.1 | 5.4 |
| | | 1.361 | 0.003 | | | 85.3 | 3.6 | | |
| P06E-055 | 21 | 0.310 | 0.004 | 0.310 | 0.002 | –185.6 | 3.2 | –186.0 | 2.2 |
| | | 0.310 | 0.003 | | | –186.3 | 3.1 | | |
| P06E-055 | 13 | 0.319 | 0.006 | 0.321 | 0.003 | - | - | - | - |
| | | 0.322 | 0.004 | | | - | - | | |
| P06E-051 | 32 | 1.330 | 0.001 | 1.332 | 0.011 | 85.9 | 3.6 | 88.9 | 4.5 |
| | | 1.346 | 0.003 | | | 92.2 | 3.8 | | |
| P06E-051 | 21 | 0.297 | 0.004 | 0.303 | 0.013 | –187.3 | 3.0 | –183.7 | 5.0 |
| | | 0.315 | 0.006 | | | –180.2 | 2.9 | | |
| P06E-051 | 13 | 0.304 | 0.001 | 0.308 | 0.013 | –196.6 | 2.9 | –195.5 | 2.1 |
| | | 0.322 | 0.002 | | | –194.3 | 3.0 | | |
| P06E-047 | 32 | 1.456 | 0.004 | 1.466 | 0.008 | 75.3 | 3.6 | 76.2 | 2.9 |
| | | 1.468 | 0.002 | | | 77.8 | 5.0 | | |
| P06E-047 | 21 | 0.313 | 0.003 | 0.326 | 0.025 | –186.7 | 3.0 | –183.9 | 4.1 |
| | | 0.348 | 0.004 | | | –180.9 | 3.1 | | |
| P06E-047 | 13 | 0.305 | 0.003 | 0.316 | 0.021 | –190.8 | 2.9 | –188.5 | 3.3 |
| | | 0.335 | 0.004 | | | –186.1 | 2.9 | | |
| P06E-043 | 32 | 1.389 | 0.004 | 1.401 | 0.021 | 85.8 | 3.5 | 87.1 | 2.9 |
| | | 1.419 | 0.005 | | | 89.7 | 5.0 | | |
| P06E-043 | 21 | 0.272 | 0.002 | 0.275 | 0.011 | - | - | - | - |
| | | 0.288 | 0.004 | | | - | - | | |
| P06E-039 | 32 | 1.326 | 0.007 | 1.365 | 0.030 | 83.1 | 2.5 | 82.2 | 1.8 |
| | | 1.368 | 0.002 | | | 81.4 | 2.6 | | |
| P06E-039 | 21 | 0.298 | 0.004 | 0.288 | 0.018 | –191.1 | 2.3 | –192.4 | 1.7 |
| | | 0.273 | 0.005 | | | –193.5 | 2.2 | | |
| P06E-039 | 13 | 0.286 | 0.002 | 0.277 | 0.020 | –196.8 | 2.2 | –195.0 | 2.3 |
| | | 0.258 | 0.003 | | | –193.5 | 2.0 | | |
| P06E-X19 | 32 | 1.515 | 0.003 | 1.521 | 0.011 | 83.8 | 3.6 | 84.0 | 2.5 |
| | | 1.531 | 0.004 | | | 84.3 | 3.6 | | |

Table 3.10.5. continued.

| Station | Btl | $\delta^{13}C$ / ‰ | | | | $\Delta^{14}C$ / ‰ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ | Error[a] | E.W.Mean[b] | Uncertainty[c] | $\Delta^{14}C$ | Error[d] | E.W.Mean[b] | Uncertainty[c] |
| P06E-X19 | 21 | 0.266 | 0.004 | 0.270 | 0.004 | –184.8 | 3.0 | –184.4 | 2.1 |
| | | 0.272 | 0.003 | | | –184.1 | 2.9 | | |
| P06E-X19 | 13 | 0.304 | 0.003 | 0.305 | 0.003 | - | - | - | - |
| | | 0.306 | 0.005 | | | - | - | | |
| P06E-031 | 32 | 1.402 | 0.004 | 1.430 | 0.030 | 80.2 | 4.1 | 82.4 | 2.9 |
| | | 1.445 | 0.003 | | | 84.4 | 4.0 | | |
| P06E-031 | 21 | 0.244 | 0.003 | 0.274 | 0.031 | –190.7 | 3.3 | –194.6 | 5.5 |
| | | 0.288 | 0.002 | | | –198.5 | 3.3 | | |
| P06E-031 | 13 | 0.276 | 0.002 | 0.290 | 0.032 | –198.4 | 3.3 | –201.8 | 4.8 |
| | | 0.321 | 0.003 | | | –205.2 | 3.3 | | |
| P06E-027 | 32 | 1.357 | 0.004 | 1.352 | 0.008 | 54.4 | 4.0 | 50.8 | 5.3 |
| | | 1.345 | 0.005 | | | 46.9 | 4.1 | | |
| P06E-027 | 21 | 0.227 | 0.002 | 0.234 | 0.009 | –212.8 | 3.5 | –210.2 | 3.5 |
| | | 0.240 | 0.002 | | | –207.8 | 3.4 | | |
| P06E-027 | 13 | 0.229 | 0.003 | 0.233 | 0.008 | –215.2 | 3.3 | –218.6 | 4.7 |
| | | 0.240 | 0.004 | | | –221.8 | 3.2 | | |
| P06E-023 | 32 | 1.310 | 0.005 | 1.316 | 0.006 | - | - | - | - |
| | | 1.318 | 0.003 | | | - | - | | |
| P06E-023 | 21 | 0.204 | 0.003 | 0.204 | 0.003 | –189.3 | 3.2 | –188.9 | 2.3 |
| | | 0.203 | 0.005 | | | –188.4 | 3.2 | | |
| P06E-019 | 32 | 0.474 | 0.003 | 0.461 | 0.025 | 21.7 | 3.5 | 22.8 | 2.5 |
| | | 0.438 | 0.004 | | | 24.0 | 3.6 | | |
| P06E-019 | 21 | 0.211 | 0.004 | 0.214 | 0.004 | –193.5 | 3.1 | –195.8 | 3.1 |
| | | 0.216 | 0.004 | | | –197.9 | 3.0 | | |
| P06E-019 | 13 | 0.206 | 0.004 | 0.210 | 0.006 | –224.3 | 3.0 | –219.8 | 6.4 |
| | | 0.215 | 0.005 | | | –215.3 | 3.0 | | |
| P06E-015 | 32 | 0.084 | 0.004 | 0.076 | 0.011 | –6.9 | 3.5 | –7.4 | 2.5 |
| | | 0.068 | 0.004 | | | –8.0 | 3.5 | | |
| P06E-015 | 21 | 0.177 | 0.005 | 0.184 | 0.013 | –207.2 | 3.2 | –206.3 | 2.2 |
| | | 0.195 | 0.006 | | | –205.4 | 3.0 | | |

Table 3.10.5. continued.

| Station | Btl | $\delta^{13}C$ / ‰ | | | | $\Delta^{14}C$ / ‰ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ | Error[a] | E.W.Mean[b] | Uncertainty[c] | $\Delta^{14}C$ | Error[d] | E.W.Mean[b] | Uncertainty[c] |
| P06E-015 | 13 | 0.249 | 0.004 | 0.246 | 0.009 | –215.0 | 2.9 | –217.7 | 3.9 |
| | | 0.236 | 0.007 | | | –220.5 | 3.0 | | |
| P06E-011 | 32 | –0.082 | 0.003 | –0.078 | 0.010 | - | - | - | - |
| | | –0.068 | 0.005 | | | - | - | | |
| P06E-011 | 21 | 0.208 | 0.003 | 0.203 | 0.014 | –200.1 | 3.1 | –199.5 | 2.1 |
| | | 0.188 | 0.005 | | | –198.9 | 2.9 | | |
| P06E-011 | 13 | 0.211 | 0.003 | 0.202 | 0.013 | - | - | - | - |
| | | 0.193 | 0.003 | | | - | - | | |
| A10-629 | 32 | 1.098 | 0.003 | 1.091 | 0.010 | - | - | - | - |
| | | 1.084 | 0.003 | | | - | - | | |
| A10-629 | 1 | - | - | - | - | –114.9 | 3.5 | –113.7 | 2.5 |
| | | - | - | | | –112.5 | 3.5 | | |
| A10-003 | 32 | 1.251 | 0.005 | 1.250 | 0.003 | 103.0 | 4.1 | 102.3 | 3.0 |
| | | 1.250 | 0.003 | | | 101.6 | 4.3 | | |
| A10-003 | 21 | 0.655 | 0.003 | 0.670 | 0.030 | –118.6 | 3.3 | –117.3 | 3.7 |
| | | 0.697 | 0.004 | | | –113.3 | 5.9 | | |
| A10-003 | 13 | 1.043 | 0.004 | 1.009 | 0.030 | –99.7 | 3.3 | –100.0 | 2.8 |
| | | 1.000 | 0.002 | | | –100.6 | 5.1 | | |
| A10-007 | 32 | 1.174 | 0.003 | 1.180 | 0.015 | 83.9 | 4.0 | 81.3 | 3.7 |
| | | 1.195 | 0.005 | | | 78.6 | 4.0 | | |
| A10-007 | 21 | 0.677 | 0.001 | 0.677 | 0.006 | –128.1 | 3.5 | –131.8 | 5.0 |
| | | 0.668 | 0.005 | | | –135.2 | 3.4 | | |
| A10-007 | 13 | 0.992 | 0.005 | 1.002 | 0.021 | –104.6 | 3.7 | –103.9 | 2.6 |
| | | 1.022 | 0.007 | | | –103.2 | 3.6 | | |
| A10-X17 | 21 | 0.694 | 0.003 | 0.686 | 0.012 | –119.3 | 3.3 | –121.7 | 3.5 |
| | | 0.677 | 0.003 | | | –124.2 | 3.3 | | |
| A10-X17 | 1 | 1.028 | 0.004 | 1.046 | 0.033 | - | - | - | - |
| | | 1.074 | 0.005 | | | - | - | | |
| A10-021 | 32 | 1.238 | 0.002 | 1.237 | 0.002 | 83.9 | 4.0 | 83.0 | 2.8 |
| | | 1.235 | 0.004 | | | 82.1 | 4.0 | | |

Table 3.10.5. continued.

| Station | Btl | $\delta^{13}C$ / ‰ | | | | $\Delta^{14}C$ / ‰ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ | Error[a] | E.W.Mean[b] | Uncertainty[c] | $\Delta^{14}C$ | Error[d] | E.W.Mean[b] | Uncertainty[c] |
| A10-029 | 32 | 1.217 | 0.002 | 1.213 | 0.026 | 88.9 | 4.1 | 90.2 | 3.7 |
| | | 1.180 | 0.006 | | | 94.1 | 7.1 | | |
| A10-029 | 21 | 0.670 | 0.003 | 0.995 | 0.004 | - | - | - | - |
| | | 0.681 | 0.003 | | | - | - | | |
| A10-035 | 21 | 0.671 | 0.003 | 0.660 | 0.016 | –120.0 | 3.3 | –117.3 | 3.8 |
| | | 0.648 | 0.003 | | | –114.6 | 3.4 | | |
| A10-035 | 13 | - | - | - | - | –107.0 | 3.3 | –103.4 | 5.1 |
| | | - | - | | | –99.8 | 3.3 | | |
| A10-038 | 32 | 1.173 | 0.004 | 1.171 | 0.004 | - | - | - | - |
| | | 1.168 | 0.004 | | | - | - | | |
| A10-038 | 21 | 0.678 | 0.004 | 0.661 | 0.019 | –123.7 | 3.3 | –120.7 | 4.2 |
| | | 0.651 | 0.003 | | | –117.7 | 3.3 | | |
| A10-X16 | 32 | 1.204 | 0.002 | 1.203 | 0.006 | 74.4 | 6.0 | 77.6 | 3.3 |
| | | 1.195 | 0.005 | | | 79.0 | 4.0 | | |
| A10-X16 | 13 | 0.983 | 0.006 | 0.935 | 0.037 | –99.1 | 3.4 | –98.5 | 2.4 |
| | | 0.930 | 0.002 | | | –97.9 | 3.4 | | |
| A10-043 | 21 | 0.648 | 0.004 | 0.654 | 0.008 | –130.0 | 3.3 | –126.9 | 4.5 |
| | | 0.660 | 0.004 | | | –123.7 | 3.4 | | |
| A10-043 | 13 | 0.954 | 0.004 | 0.935 | 0.021 | –98.2 | 3.3 | –103.9 | 8.6 |
| | | 0.924 | 0.003 | | | –110.4 | 3.5 | | |
| A10-X15 | 32 | 1.233 | 0.002 | 1.209 | 0.034 | 88.3 | 3.9 | 83.9 | 6.4 |
| | | 1.185 | 0.002 | | | 79.3 | 4.0 | | |
| A10-X15 | 13 | 0.927 | 0.004 | 0.950 | 0.032 | –113.1 | 3.6 | –113.7 | 2.5 |
| | | 0.972 | 0.004 | | | –114.3 | 3.4 | | |
| A10-051 | 32 | 1.092 | 0.004 | 1.123 | 0.034 | 70.3 | 3.9 | 70.3 | 2.8 |
| | | 1.140 | 0.003 | | | 70.3 | 3.9 | | |
| A10-051 | 21 | 0.576 | 0.002 | 0.581 | 0.025 | –127.9 | 3.2 | –123.2 | 7.0 |
| | | 0.612 | 0.005 | | | –118.0 | 3.4 | | |
| A10-055 | 21 | 0.600 | 0.003 | 0.574 | 0.037 | –121.2 | 3.6 | –119.5 | 2.5 |
| | | 0.548 | 0.003 | | | –117.8 | 3.6 | | |

Table 3.10.5. continued.

| Station | Btl | $\delta^{13}C$ / ‰ | | | | $\Delta^{14}C$ / ‰ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ | Error[a] | E.W.Mean[b] | Uncertainty[c] | $\Delta^{14}C$ | Error[d] | E.W.Mean[b] | Uncertainty[c] |
| A10-059 | 32 | 1.191 | 0.002 | 1.190 | 0.002 | 71.6 | 3.8 | 74.4 | 6.6 |
| | | 1.188 | 0.003 | | | 80.9 | 5.8 | | |
| A10-059 | 13 | 0.880 | 0.003 | 0.871 | 0.009 | –111.2 | 3.4 | –112.2 | 2.9 |
| | | 0.867 | 0.002 | | | –114.9 | 5.4 | | |
| A10-X14 | 32 | 1.219 | 0.005 | 1.215 | 0.004 | - | - | - | - |
| | | 1.214 | 0.003 | | | - | - | | |
| A10-X14 | 21 | 0.623 | 0.003 | 0.580 | 0.044 | –120.9 | 3.5 | –116.7 | 5.7 |
| | | 0.561 | 0.002 | | | –112.8 | 3.4 | | |
| A10-067 | 21 | 0.618 | 0.003 | 0.595 | 0.033 | –129.4 | 3.4 | –125.1 | 5.5 |
| | | 0.571 | 0.003 | | | –121.6 | 3.1 | | |
| A10-067 | 13 | 0.904 | 0.002 | 0.893 | 0.016 | –115.7 | 3.4 | –117.1 | 2.4 |
| | | 0.882 | 0.002 | | | –118.5 | 3.4 | | |
| A10-071 | 32 | 0.917 | 0.003 | 0.925 | 0.011 | 89.6 | 3.7 | 88.2 | 2.7 |
| | | 0.933 | 0.003 | | | 86.7 | 3.8 | | |
| A10-071 | 13 | 0.874 | 0.004 | 0.872 | 0.002 | –118.4 | 3.5 | –112.6 | 7.4 |
| | | 0.872 | 0.002 | | | –107.9 | 3.2 | | |
| A10-075 | 32 | 1.030 | 0.003 | 1.034 | 0.006 | 94.3 | 3.8 | 93.4 | 2.7 |
| | | 1.038 | 0.003 | | | 92.5 | 3.7 | | |
| A10-075 | 21 | 0.661 | 0.007 | 0.649 | 0.010 | –122.3 | 3.3 | –122.1 | 2.3 |
| | | 0.647 | 0.003 | | | –121.9 | 3.3 | | |
| A10-079 | 21 | 0.653 | 0.002 | 0.655 | 0.010 | - | - | - | - |
| | | 0.667 | 0.005 | | | - | - | | |
| A10-079 | 13 | 0.846 | 0.004 | 0.850 | 0.005 | –128.8 | 3.4 | –123.8 | 6.8 |
| | | 0.853 | 0.004 | | | –119.2 | 3.3 | | |
| A10-083 | 32 | 1.042 | 0.002 | 1.035 | 0.016 | - | - | - | - |
| | | 1.020 | 0.003 | | | - | - | | |
| A10-083 | 13 | 0.852 | 0.002 | 0.850 | 0.004 | –117.2 | 3.3 | –114.4 | 4.2 |
| | | 0.847 | 0.003 | | | –111.3 | 3.5 | | |
| A10-087 | 32 | 1.034 | 0.005 | 1.027 | 0.006 | - | - | - | - |
| | | 1.026 | 0.002 | | | - | - | | |

Table 3.10.5. continued.

| Station | Btl | $\delta^{13}C$ / ‰ | | | | $\Delta^{14}C$ / ‰ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ | Error[a] | E.W.Mean[b] | Uncertainty[c] | $\Delta^{14}C$ | Error[d] | E.W.Mean[b] | Uncertainty[c] |
| A10-087 | 1 | 0.593 | 0.004 | 0.591 | 0.004 | –126.1 | 3.4 | –123.5 | 3.6 |
| | | 0.587 | 0.005 | | | –121.0 | 3.4 | | |
| A10-093 | 32 | 1.032 | 0.005 | 1.026 | 0.007 | 74.6 | 4.0 | 81.1 | 9.5 |
| | | 1.022 | 0.004 | | | 88.0 | 4.1 | | |
| A10-093 | 21 | - | - | - | - | –124.2 | 5.3 | –119.7 | 4.5 |
| | | - | - | | | –117.8 | 3.5 | | |
| A10-093 | 13 | 0.877 | 0.003 | 0.882 | 0.007 | –114.5 | 3.7 | –113.8 | 2.5 |
| | | 0.887 | 0.003 | | | –113.3 | 3.5 | | |
| I04-601 | 21 | 0.683 | 0.005 | 0.683 | 0.004 | –141.4 | 3.1 | –141.2 | 2.3 |
| | | 0.683 | 0.007 | | | –140.8 | 3.3 | | |
| I04-601 | 13 | 0.681 | 0.003 | 0.696 | 0.015 | –144.0 | 3.3 | –147.0 | 4.2 |
| | | 0.702 | 0.002 | | | –150.0 | 3.3 | | |
| I04-595 | 32 | 0.671 | 0.006 | 0.632 | 0.047 | 67.4 | 3.8 | 64.9 | 3.6 |
| | | 0.605 | 0.005 | | | 62.3 | 3.9 | | |
| I04-595 | 13 | 0.723 | 0.005 | 0.705 | 0.018 | –142.6 | 3.2 | –144.3 | 2.3 |
| | | 0.698 | 0.003 | | | –145.8 | 3.1 | | |
| I04-589 | 32 | - | - | - | - | 80.2 | 3.7 | 81.7 | 2.7 |
| | | - | - | | | 83.3 | 3.8 | | |
| I04-589 | 21 | 0.377 | 0.002 | 0.378 | 0.004 | –153.3 | 4.3 | –150.4 | 3.2 |
| | | 0.382 | 0.004 | | | –148.7 | 3.3 | | |
| I03-557 | 21 | 0.467 | 0.003 | 0.469 | 0.008 | –165.7 | 3.0 | –163.9 | 2.5 |
| | | 0.479 | 0.006 | | | –162.2 | 3.0 | | |
| I03-557 | 13 | 0.293 | 0.004 | 0.288 | 0.008 | –184.3 | 3.0 | –184.9 | 2.2 |
| | | 0.281 | 0.005 | | | –185.7 | 3.2 | | |
| I03-551 | 13 | 0.339 | 0.003 | 0.333 | 0.012 | –190.5 | 3.0 | –189.7 | 2.2 |
| | | 0.322 | 0.004 | | | –188.9 | 3.1 | | |
| I03-545 | 32 | 0.512 | 0.006 | 0.502 | 0.010 | 51.4 | 3.5 | 49.5 | 2.8 |
| | | 0.498 | 0.004 | | | 47.4 | 3.6 | | |
| I03-545 | 21 | 0.416 | 0.001 | 0.418 | 0.008 | –153.9 | 3.0 | –156.4 | 3.7 |
| | | 0.427 | 0.002 | | | –159.2 | 3.1 | | |

Table 3.10.5. continued.

| Station | Btl | $\delta^{13}C$ / ‰ | | | | $\Delta^{14}C$ / ‰ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ | Error[a] | E.W.Mean[b] | Uncertainty[c] | $\Delta^{14}C$ | Error[d] | E.W.Mean[b] | Uncertainty[c] |
| I03-535 | 21 | 0.384 | 0.003 | 0.383 | 0.003 | –172.6 | 3.1 | –168.4 | 6.0 |
| | | 0.380 | 0.004 | | | –164.1 | 3.2 | | |
| I03-535 | 13 | 0.378 | 0.003 | 0.379 | 0.003 | –186.1 | 3.3 | –185.9 | 2.3 |
| | | 0.382 | 0.004 | | | –185.7 | 3.3 | | |
| I03-531 | 32 | 0.735 | 0.006 | 0.679 | 0.044 | 67.3 | 3.9 | 64.1 | 4.5 |
| | | 0.673 | 0.002 | | | 61.0 | 3.8 | | |
| I03-531 | 13 | 0.380 | 0.004 | 0.379 | 0.003 | –172.9 | 3.2 | –171.8 | 2.3 |
| | | 0.377 | 0.005 | | | –170.8 | 3.3 | | |
| I03-525 | 32 | 0.860 | 0.005 | 0.870 | 0.013 | 68.9 | 3.7 | 63.9 | 6.9 |
| | | 0.879 | 0.005 | | | 59.2 | 3.6 | | |
| I03-519 | 21 | - | - | - | - | –167.6 | 3.1 | –172.1 | 6.2 |
| | | - | - | | | –176.4 | 3.0 | | |
| I03-513 | 32 | 0.736 | 0.003 | 0.712 | 0.035 | - | - | - | - |
| | | 0.687 | 0.003 | | | - | - | | |
| I03-513 | 21 | 0.274 | 0.004 | 0.244 | 0.026 | –170.2 | 2.9 | –167.6 | 3.7 |
| | | 0.237 | 0.002 | | | –165.0 | 2.9 | | |
| I03-507 | 21 | 0.234 | 0.003 | 0.222 | 0.017 | –163.5 | 3.1 | –168.8 | 7.6 |
| | | 0.210 | 0.003 | | | –174.3 | 3.2 | | |
| I03-507 | 13 | 0.435 | 0.003 | 0.432 | 0.003 | –175.9 | 3.3 | –179.2 | 4.5 |
| | | 0.431 | 0.002 | | | –182.2 | 3.2 | | |
| I03-503 | 32 | 0.825 | 0.002 | 0.823 | 0.004 | 75.0 | 3.6 | 75.9 | 2.6 |
| | | 0.819 | 0.003 | | | 76.8 | 3.8 | | |
| I03-503 | 13 | 0.415 | 0.005 | 0.433 | 0.021 | –184.7 | 3.0 | –183.5 | 2.1 |
| | | 0.445 | 0.004 | | | –182.3 | 3.0 | | |
| I03-X08 | 32 | 0.869 | 0.004 | 0.846 | 0.017 | 61.8 | 3.5 | 61.6 | 2.5 |
| | | 0.845 | 0.001 | | | 61.3 | 3.5 | | |
| I03-X08 | 21 | 0.255 | 0.001 | 0.255 | 0.006 | –175.6 | 3.1 | –176.1 | 2.2 |
| | | 0.264 | 0.005 | | | –176.6 | 3.1 | | |
| I03-495 | 21 | 0.308 | 0.005 | 0.307 | 0.003 | –174.6 | 3.0 | –177.9 | 4.6 |
| | | 0.306 | 0.004 | | | –181.1 | 3.0 | | |

Table 3.10.5. continued.

| Station | Btl | $\delta^{13}C$ / ‰ | | | | $\Delta^{14}C$ / ‰ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ | Error[a] | E.W.Mean[b] | Uncertainty[c] | $\Delta^{14}C$ | Error[d] | E.W.Mean[b] | Uncertainty[c] |
| I03-495 | 13 | - | - | - | - | –186.1 | 3.0 | –183.0 | 4.5 |
| | | - | - | | | –179.8 | 3.0 | | |
| I03-491 | 32 | 0.856 | 0.003 | 0.854 | 0.002 | 68.4 | 3.7 | 70.2 | 2.6 |
| | | 0.853 | 0.002 | | | 72.0 | 3.6 | | |
| I03-491 | 13 | 0.415 | 0.002 | 0.414 | 0.003 | –184.2 | 3.1 | –182.7 | 2.3 |
| | | 0.411 | 0.003 | | | –181.0 | 3.2 | | |
| I03-487 | 1 | 0.304 | 0.005 | 0.324 | 0.019 | –179.1 | 3.3 | –180.6 | 2.3 |
| | | 0.331 | 0.003 | | | –181.8 | 3.1 | | |
| I03-480 | 32 | 0.934 | 0.008 | 0.926 | 0.007 | 65.7 | 3.7 | 66.4 | 2.6 |
| | | 0.924 | 0.004 | | | 67.1 | 3.6 | | |
| I03-480 | 21 | 0.287 | 0.004 | 0.291 | 0.006 | –180.8 | 3.1 | –179.6 | 2.2 |
| | | 0.295 | 0.004 | | | –178.3 | 3.2 | | |
| I03-474 | 32 | 0.845 | 0.003 | 0.852 | 0.014 | 63.5 | 3.6 | 66.4 | 4.1 |
| | | 0.865 | 0.004 | | | 69.3 | 3.6 | | |
| I03-474 | 13 | 0.362 | 0.003 | 0.351 | 0.008 | –190.3 | 2.8 | –193.1 | 4.1 |
| | | 0.350 | 0.001 | | | –196.1 | 2.9 | | |
| I03-470 | 32 | 0.785 | 0.007 | 0.764 | 0.018 | 77.6 | 3.4 | 78.4 | 2.4 |
| | | 0.760 | 0.003 | | | 79.3 | 3.3 | | |
| I03-470 | 21 | 0.290 | 0.003 | 0.293 | 0.008 | –171.4 | 2.9 | –170.9 | 2.1 |
| | | 0.302 | 0.005 | | | –170.4 | 2.9 | | |
| I03-466 | 21 | 0.255 | 0.005 | 0.257 | 0.003 | –177.6 | 3.1 | –175.8 | 2.6 |
| | | 0.259 | 0.004 | | | –173.9 | 3.1 | | |
| I03-466 | 13 | 0.326 | 0.006 | 0.352 | 0.027 | –196.7 | 2.9 | –194.5 | 3.3 |
| | | 0.364 | 0.004 | | | –192.0 | 3.0 | | |
| I03-463 | 32 | 0.717 | 0.005 | 0.695 | 0.016 | 71.4 | 3.5 | 73.0 | 2.5 |
| | | 0.694 | 0.001 | | | 74.7 | 3.5 | | |
| I03-463 | 1 | 0.318 | 0.004 | 0.325 | 0.013 | –183.9 | 3.1 | –183.6 | 2.2 |
| | | 0.337 | 0.005 | | | –183.3 | 3.0 | | |
| I03-459 | 32 | 0.788 | 0.004 | 0.775 | 0.015 | 57.3 | 3.7 | 62.6 | 7.2 |
| | | 0.767 | 0.003 | | | 67.5 | 3.6 | | |

Table 3.10.5. continued.

| Station | Btl | $\delta^{13}C$ / ‰ | | | | $\Delta^{14}C$ / ‰ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ | Error[a] | E.W.Mean[b] | Uncertainty[c] | $\Delta^{14}C$ | Error[d] | E.W.Mean[b] | Uncertainty[c] |
| I03-459 | 21 | 0.277 | 0.004 | 0.280 | 0.004 | –187.8 | 3.1 | –180.5 | 10.3 |
| | | 0.282 | 0.003 | | | –173.2 | 3.1 | | |
| I03-459 | 13 | 0.397 | 0.003 | 0.374 | 0.045 | –190.3 | 3.1 | –188.8 | 2.7 |
| | | 0.334 | 0.004 | | | –186.5 | 3.9 | | |
| I03-455 | 32 | - | - | - | - | 38.0 | 3.7 | 43.0 | 7.2 |
| | | - | - | | | 48.2 | 3.8 | | |
| I03-455 | 21 | 0.284 | 0.005 | 0.269 | 0.022 | –192.9 | 3.1 | –188.3 | 6.5 |
| | | 0.253 | 0.005 | | | –183.7 | 3.1 | | |
| I03-455 | 13 | 0.349 | 0.001 | 0.343 | 0.042 | –186.1 | 3.1 | –186.5 | 2.2 |
| | | 0.290 | 0.003 | | | –187.0 | 3.2 | | |
| I03-451 | 32 | 0.826 | 0.004 | 0.825 | 0.003 | - | - | - | - |
| | | 0.824 | 0.006 | | | - | - | | |
| I03-451 | 21 | - | - | - | - | –177.7 | 3.2 | –177.0 | 2.3 |
| | | - | - | | | –176.4 | 3.2 | | |
| I03-451 | 13 | - | - | - | - | –189.5 | 3.2 | –192.5 | 4.3 |
| | | - | - | | | –195.6 | 3.2 | | |

a. Standard deviation of repeat measurements.
b. Error weighted mean of the replicate pair.
c. Larger of the standard deviation and the error weighted standard deviation of the replicate pair.
d. Larger of the standard deviation of repeat measurements and the counting errors.

**(7) Duplicate measurements**

At 48 stations, seawater samples were taken from two X-Niskin bottles that were collected at same depth (duplicate sampling). Most of the duplicate samples were collected in deep layers below 1,000 dbar. Results of the duplicate pair analyses are shown in Table 3.10.6. The standard deviations of the $\delta^{13}C$ and $\Delta^{14}C$ duplicate analyses in good measurement were calculated to be 0.014 ‰ (n = 39) and 3.7 ‰ (n = 40), respectively. These deviations are almost same as those obtained by the replicate analyses (0.020 ‰ for $\delta^{13}C$ and 3.9 ‰ for $\Delta^{14}C$). The results of replicate and duplicate measurements suggested that "reproducibilities" of our $\delta^{13}C$ and $\Delta^{14}C$ measurements including errors due to the sample preparation were less than 0.02 ‰ and 4 ‰, respectively.

Table 3.10.6. Summary of duplicate analyses.

| Station | Btl | $\delta^{13}C$ / ‰ | | | | $\Delta^{14}C$ / ‰ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ | Error[a] | E.W.Mean[b] | Uncertainty[c] | $\Delta^{14}C$ | Error[d] | E.W.Mean[b] | Uncertainty[c] |
| P06W-201 | 35 | 1.206 | 0.002 | 1.201 | 0.024 | 91.5 | 3.9 | 87.7 | 5.4 |
| | 16 | 1.172 | 0.005 | | | 83.9 | 3.9 | | |
| P06E-039 | 22 | 0.321 | 0.001 | 0.320 | 0.006 | –196.6 | 2.5 | –193.6 | 3.7 |
| | 11 | 0.313 | 0.003 | | | –191.3 | 2.2 | | |
| P06E-X19 | 20 | 0.274 | 0.002 | 0.278 | 0.006 | –190.4 | 3.0 | –191.2 | 2.1 |
| | 11 | 0.282 | 0.002 | | | –191.9 | 3.0 | | |
| P06E-027 | 16 | 0.274 | 0.006 | 0.256 | 0.016 | –208.7 | 3.2 | –210.7 | 2.9 |
| | 10 | 0.252 | 0.003 | | | –212.8 | 3.3 | | |
| P06E-023 | 14 | 0.201 | 0.004 | 0.200 | 0.002 | –210.0 | 3.1 | –213.7 | 5.2 |
| | 1 | 0.199 | 0.003 | | | –217.3 | 3.1 | | |
| P06E-019 | 12 | 0.250 | 0.004 | 0.236 | 0.016 | –218.0 | 3.0 | –217.2 | 2.1 |
| | 1 | 0.228 | 0.003 | | | –216.4 | 2.9 | | |
| A10-629 | 21 | 1.035 | 0.003 | 1.026 | 0.018 | - | - | - | - |
| | 17 | 1.010 | 0.004 | | | - | - | | |
| A10-007 | 16 | 1.014 | 0.004 | 0.994 | 0.018 | –99.6 | 3.6 | –101.2 | 2.5 |
| | 15 | 0.989 | 0.002 | | | –102.9 | 3.6 | | |
| A10-X17 | 13 | 0.727 | 0.006 | 0.729 | 0.004 | –136.5 | 3.3 | –136.5 | 2.3 |
| | 9 | 0.730 | 0.006 | | | –136.6 | 3.3 | | |
| A10-021 | 17 | 0.882 | 0.004 | 0.876 | 0.011 | –126.8 | 3.4 | –125.2 | 2.4 |
| | 8 | 0.866 | 0.005 | | | –123.6 | 3.5 | | |
| A10-035 | 23 | 0.974 | 0.005 | 0.967 | 0.006 | - | - | - | - |
| | 13 | 0.965 | 0.003 | | | - | - | | |
| A10-038 | 22 | 0.639 | 0.002 | 0.634 | 0.011 | - | - | - | - |
| | 4 | 0.623 | 0.003 | | | - | - | | |
| A10-X16 | 21 | 0.664 | 0.005 | 0.651 | 0.013 | - | - | - | - |
| | 8 | 0.646 | 0.003 | | | - | - | | |
| A10-043 | 20 | 0.650 | 0.003 | 0.668 | 0.018 | –145.2 | 3.5 | –146.6 | 2.4 |
| | 7 | 0.676 | 0.002 | | | –147.9 | 3.4 | | |
| A10-X15 | 18 | 0.794 | 0.003 | 0.805 | 0.016 | –124.5 | 3.4 | –122.8 | 2.4 |
| | 9 | 0.816 | 0.003 | | | –121.3 | 3.3 | | |
| A10-051 | 16 | 0.880 | 0.005 | 0.869 | 0.016 | –117.3 | 3.4 | –116.1 | 2.5 |
| | 11 | 0.858 | 0.005 | | | –114.9 | 3.6 | | |

Table 3.10.6. continued.

| Station | Btl | $\delta^{13}C$ / ‰ | | | | $\Delta^{14}C$ / ‰ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ | Error[a] | E.W.Mean[b] | Uncertainty[c] | $\Delta^{14}C$ | Error[d] | E.W.Mean[b] | Uncertainty[c] |
| A10-055 | 17 | 0.796 | 0.002 | 0.801 | 0.007 | - | - | - | - |
| | 14 | 0.806 | 0.002 | | | - | - | | |
| A10-059 | 12 | - | - | - | - | –105.9 | 3.5 | –106.5 | 2.5 |
| | 11 | - | - | | | –107.3 | 3.6 | | |
| A10-X14 | 10 | 0.844 | 0.002 | 0.885 | 0.036 | –105.0 | 3.5 | –107.9 | 4.2 |
| | 1 | 0.895 | 0.001 | | | –110.9 | 3.5 | | |
| A10-067 | 9 | 0.884 | 0.004 | 0.867 | 0.025 | –111.8 | 3.3 | –113.0 | 2.3 |
| | 8 | 0.849 | 0.004 | | | –114.3 | 3.2 | | |
| A10-071 | 7 | 0.788 | 0.004 | 0.793 | 0.006 | –121.3 | 3.4 | –117.9 | 4.7 |
| | 6 | 0.797 | 0.004 | | | –114.7 | 3.3 | | |
| A10-075 | 11 | 0.842 | 0.001 | 0.846 | 0.013 | –125.9 | 3.5 | –121.7 | 5.6 |
| | 4 | 0.860 | 0.002 | | | –118.0 | 3.3 | | |
| A10-079 | 7 | - | - | - | - | –148.5 | 3.4 | –150.9 | 3.4 |
| | 2 | - | - | | | –153.3 | 3.3 | | |
| A10-083 | 23 | 0.554 | 0.005 | 0.546 | 0.009 | - | - | - | - |
| | 5 | 0.541 | 0.004 | | | - | - | | |
| A10-087 | 21 | 0.576 | 0.002 | 0.553 | 0.021 | - | - | - | - |
| | 5 | 0.547 | 0.001 | | | - | - | | |
| A10-093 | 12 | 0.855 | 0.003 | 0.835 | 0.021 | - | - | - | - |
| | 8 | 0.826 | 0.002 | | | - | - | | |
| I04-601 | 21 | 0.683 | 0.004 | 0.684 | 0.002 | –141.2 | 2.3 | –141.1 | 1.8 |
| | 14 | 0.684 | 0.002 | | | –141.0 | 3.2 | | |
| I04-595 | 18 | 0.668 | 0.003 | 0.676 | 0.016 | –137.5 | 3.3 | –142.8 | 7.1 |
| | 12 | 0.690 | 0.004 | | | –147.6 | 3.2 | | |
| I04-589 | 15 | - | - | - | - | –142.7 | 3.1 | –142.8 | 2.2 |
| | 11 | - | - | | | –142.9 | 3.1 | | |
| I03-557 | 10 | 0.474 | 0.002 | 0.480 | 0.015 | –174.8 | 3.1 | –170.7 | 5.6 |
| | 8 | 0.495 | 0.003 | | | –166.9 | 3.0 | | |
| I03-551 | 7 | 0.502 | 0.008 | 0.490 | 0.010 | –161.3 | 3.1 | –160.2 | 2.3 |
| | 6 | 0.488 | 0.003 | | | –159.0 | 3.3 | | |
| I03-545 | 8 | - | - | - | - | –170.5 | 3.2 | –168.7 | 2.5 |
| | 4 | - | - | | | –166.9 | 3.2 | | |

Table 3.10.6. continued.

| Station | Btl | $\delta^{13}C$ / ‰ | | | | $\Delta^{14}C$ / ‰ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ | Error[a] | E.W.Mean[b] | Uncertainty[c] | $\Delta^{14}C$ | Error[d] | E.W.Mean[b] | Uncertainty[c] |
| I03-535 | 22 | 0.444 | 0.004 | 0.424 | 0.015 | –167.0 | 3.1 | –171.0 | 5.7 |
| | 7 | 0.423 | 0.001 | | | –175.1 | 3.1 | | |
| I03-535 | 23 | 0.622 | 0.005 | 0.637 | 0.021 | –125.8 | 3.4 | –123.7 | 3.0 |
| | 3 | 0.652 | 0.005 | | | –121.6 | 3.4 | | |
| I03-525 | 17 | - | - | - | - | –177.9 | 3.0 | –176.8 | 2.2 |
| | 14 | - | - | | | –175.8 | 3.1 | | |
| I03-519 | 16 | 0.445 | 0.002 | 0.446 | 0.004 | –162.9 | 3.0 | –165.1 | 3.0 |
| | 14 | 0.451 | 0.004 | | | –167.2 | 3.0 | | |
| I03-513 | 11 | - | - | - | - | –177.1 | 3.0 | –176.6 | 2.1 |
| | 9 | - | - | | | –176.2 | 2.9 | | |
| I03-507 | 8 | - | - | - | - | –193.3 | 3.1 | –189.1 | 6.1 |
| | 6 | - | - | | | –184.6 | 3.2 | | |
| I03-503 | 6 | 0.411 | 0.003 | 0.396 | 0.022 | –189.7 | 2.9 | –189.4 | 2.1 |
| | 1 | 0.380 | 0.003 | | | –189.0 | 2.9 | | |
| I03-X08 | 6 | 0.357 | 0.003 | 0.364 | 0.009 | –191.3 | 2.9 | –189.2 | 3.3 |
| | 4 | 0.370 | 0.003 | | | –186.7 | 3.1 | | |
| I03-495 | 5 | - | - | - | - | –187.6 | 3.0 | –186.8 | 2.1 |
| | 2 | - | - | | | –186.0 | 3.0 | | |
| I03-491 | 23 | 0.381 | 0.002 | 0.384 | 0.003 | –193.5 | 3.0 | –191.5 | 2.9 |
| | 6 | 0.385 | 0.001 | | | –189.4 | 3.1 | | |
| I03-487 | 21 | 0.321 | 0.003 | 0.322 | 0.002 | –189.4 | 3.1 | –188.9 | 2.2 |
| | 19 | 0.322 | 0.003 | | | –188.4 | 3.1 | | |
| I03-480 | 18 | 0.484 | 0.004 | 0.481 | 0.004 | –179.2 | 3.2 | –175.7 | 5.1 |
| | 4 | 0.478 | 0.004 | | | –172.0 | 3.3 | | |
| I03-474 | 16 | - | - | - | - | –163.7 | 2.8 | –170.0 | 9.3 |
| | 6 | - | - | | | –176.8 | 2.9 | | |
| I03-470 | 14 | 0.451 | 0.002 | 0.453 | 0.006 | –161.8 | 2.9 | –162.6 | 2.0 |
| | 4 | 0.459 | 0.003 | | | –163.4 | 2.8 | | |
| I03-463 | 13 | 0.430 | 0.004 | 0.434 | 0.004 | –170.1 | 2.9 | –166.9 | 5.1 |
| | 3 | 0.436 | 0.003 | | | –162.9 | 3.2 | | |
| I03-455 | 10 | 0.437 | 0.004 | 0.436 | 0.003 | –176.2 | 3.2 | –173.8 | 3.3 |
| | 5 | 0.434 | 0.004 | | | –171.6 | 3.1 | | |

a. Standard deviation of repeat measurements.
b. Error weighted mean of the replicate pair.
c. Larger of the standard deviation and the error weighted standard deviation of the replicate pair.
d. Larger of the standard deviation of repeat measurements and the counting errors.

**(8) Reference seawater measurements**

During the sample measurements period from May 2004 to October 2006, we synchronously carried out $\delta^{13}C$ and $\Delta^{14}C$ measurements of reference seawaters. The reference seawater was prepared from a large volume of surface seawater collected in open ocean. The surface seawater was filtered, exposed to ultraviolet irradiation, poisoned by $HgCl_2$, and then dispensed in 250 $cm^3$ glass bottles. The $\delta^{13}C$ and $\Delta^{14}C$ of the reference seawater was measured at every 40 samples analyses approximately. The results are shown in Figure 3.10.2 and Table 3.10.7. The standard deviations of $\delta^{13}C$ and $\Delta^{14}C$ were 0.027 ‰ and 5.8 ‰, respectively. These deviations were slightly larger than those obtained by the replicate and duplicate measurements (0.02 ‰ for $\delta^{13}C$ and 4 ‰ for $\Delta^{14}C$). Finally we concluded that "precisions" of our $\delta^{13}C$ and $\Delta^{14}C$ analyses including error due to the sample preparation and storage were about 0.03 ‰ and 6 ‰, respectively.

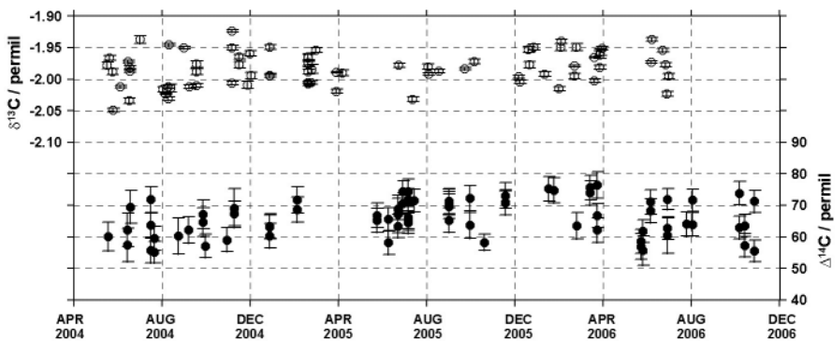


Figure 3.10.2. $\delta^{13}C$ (open circles) and $\Delta^{14}C$ (closed circles) measurements of the reference seawaters.

Table 3.10.7. Summary of reference seawaters measurements.

| No. | RS No. | $\delta^{13}C$ / ‰ | | | $\Delta^{14}C$[a] / ‰ | | |
|---|---|---|---|---|---|---|---|
| | | Measurement date | $\delta^{13}C$ | Error[b] | Measurement date | $\Delta^{14}C$ | Error[c] |
| 1 | RM0204-026 | 17-May-04 | –1.978 | 0.005 | 18-May-04 | 60.2 | 4.6 |
| 2 | RM0204-156 | 20-May-04 | –1.966 | 0.004 | 14-Jun-04 | 62.3 | 5.3 |
| 3 | RM0204-093 | 24-May-04 | –1.988 | 0.005 | 14-Jun-04 | 57.5 | 5.3 |
| 4 | RM0204-103 | 25-May-04 | –2.049 | 0.003 | 18-Jun-04 | 69.5 | 5.2 |
| 5 | RM0204-028 | 04-Jun-04 | –2.012 | 0.002 | 16-Jul-04 | 71.9 | 4.1 |
| 6 | RM0204-148 | 15-Jun-04 | –1.972 | 0.002 | 16-Jul-04 | 55.7 | 3.9 |
| 7 | RM0204-022 | 16-Jun-04 | –2.034 | 0.004 | 16-Jul-04 | 63.8 | 3.8 |
| 8 | RM0204-152 | 17-Jun-04 | –1.987 | 0.002 | 21-Jul-04 | 55.2 | 3.5 |
| 9 | RM0204-064 | 01-Jul-04 | –1.937 | 0.006 | 21-Jul-04 | 59.6 | 3.8 |
| 10 | RM0204-076 | 02-Aug-04 | –2.016 | 0.004 | 23-Aug-04 | 60.3 | 5.7 |
| 11 | RM0204-115 | 05-Aug-04 | –2.023 | 0.001 | 06-Sep-04 | 62.2 | 4.2 |
| 12 | RM0204-092 | 10-Aug-04 | –1.945 | 0.002 | 26-Sep-04 | 67.2 | 4.6 |
| 13 | RM0204-027 | 12-Aug-04 | –2.014 | 0.006 | 26-Sep-04 | 64.7 | 4.5 |
| 14 | RM0204-018 | 31-Aug-04 | –1.950 | 0.002 | 29-Sep-04 | 57.1 | 3.7 |
| 15 | RM0204-169 | 17-Jun-04 | –1.981 | 0.002 | 29-Oct-04 | 59.2 | 3.8 |
| 16 | RM0204-062 | 12-Jul-05 | –2.032 | 0.004 | 08-Nov-04 | 69.2 | 6.2 |
| 17 | RM0204-048 | 09-Aug-04 | –2.031 | 0.003 | 08-Nov-04 | 67.5 | 3.9 |
| 18 | RM0204-004 | 15-Nov-04 | –1.977 | 0.005 | 27-Dec-04 | 60.5 | 3.9 |
| 19 | RM0204-119 | 26-Nov-04 | –2.009 | 0.006 | 27-Dec-04 | 63.5 | 3.9 |
| 20 | RM0204-108 | 09-Aug-04 | –2.012 | 0.003 | 27-Dec-04 | 63.3 | 3.8 |
| 21 | RM0204-123 | 30-Nov-04 | –1.959 | 0.004 | 03-Feb-05 | 68.8 | 4.0 |
| 22 | RM0204-065 | 01-Dec-04 | –1.994 | 0.005 | 03-Feb-05 | 71.8 | 4.2 |
| 23 | RM0204-159 | 22-Feb-05 | –2.005 | 0.003 | 24-May-05 | 65.3 | 3.8 |
| 24 | RM0204-055 | 18-Feb-05 | –1.966 | 0.006 | 24-May-05 | 66.9 | 3.9 |
| 25 | RM0204-177 | 23-Feb-05 | –1.984 | 0.007 | 09-Jun-05 | 58.3 | 3.7 |
| 26 | RM0204-111 | 01-Mar-05 | –1.954 | 0.004 | 09-Jun-05 | 65.7 | 3.6 |
| 27 | RM0204-138 | 07-Sep-04 | –2.012 | 0.003 | 22-Jun-05 | 69.0 | 3.5 |
| 28 | RM0204-058 | 17-Sep-04 | –2.010 | 0.003 | 22-Jun-05 | 63.5 | 3.7 |
| 29 | RM0204-165 | 17-Sep-04 | –1.976 | 0.005 | 22-Jun-05 | 67.3 | 6.0 |
| 30 | RM0204-183 | 17-Sep-04 | –1.988 | 0.005 | 29-Jun-05 | 70.7 | 3.5 |

Table 3.10.7. continued.

| No. | RS No. | $\delta^{13}C$ / ‰ | | | $\Delta^{14}C^{a}$ / ‰ | | |
|---|---|---|---|---|---|---|---|
| | | Measurement date | $\delta^{13}C$ | Error[b] | Measurement date | $\Delta^{14}C$ | Error[c] |
| 31 | RM0204-135 | 05-Nov-04 | –2.006 | 0.003 | 29-Jun-05 | 74.4 | 3.6 |
| 32 | RM0204-070 | 05-Nov-04 | –1.923 | 0.002 | 06-Jul-05 | 65.9 | 3.8 |
| 33 | RM0204-081 | 05-Nov-04 | –1.950 | 0.004 | 06-Jul-05 | 71.5 | 3.8 |
| 34 | RM0204-179 | 15-Nov-04 | –1.964 | 0.004 | 06-Jul-05 | 74.4 | 4.0 |
| 35 | RM0204-016 | 27-Dec-04 | –1.949 | 0.004 | 06-Jul-05 | 72.0 | 3.5 |
| 36 | RM0204-075 | 27-Dec-04 | –1.995 | 0.002 | 06-Jul-05 | 66.4 | 3.7 |
| 37 | RM0204-133 | 27-Dec-04 | –1.994 | 0.003 | 06-Jul-05 | 64.7 | 3.6 |
| 38 | RM0204-098 | 18-Feb-05 | –2.007 | 0.003 | 14-Jul-05 | 71.6 | 3.6 |
| 39 | RM0204-087 | 18-Feb-05 | –1.964 | 0.005 | 19-Oct-05 | 58.5 | 2.5 |
| 40 | RM0204-014 | 18-Feb-05 | –1.988 | 0.004 | 31-Aug-05 | 71.1 | 3.5 |
| 41 | RM0204-182 | 18-Feb-05 | –1.975 | 0.005 | 31-Aug-05 | 71.5 | 4.1 |
| 42 | RM0204-145 | 18-Feb-05 | –2.005 | 0.002 | 31-Aug-05 | 69.9 | 3.9 |
| 43 | RM0204-106 | 18-Feb-05 | –1.974 | 0.004 | 31-Aug-05 | 65.5 | 3.9 |
| 44 | RM0204-035 | 29-Mar-05 | –1.989 | 0.001 | 31-Aug-05 | 71.2 | 4.1 |
| 45 | RM0204-147 | 29-Mar-05 | –2.019 | 0.003 | 29-Sep-05 | 63.9 | 4.1 |
| 46 | RM0204-061 | 06-Apr-05 | –1.990 | 0.005 | 29-Sep-05 | 72.5 | 4.0 |
| 47 | RM0204-132 | 23-Jun-05 | –1.978 | 0.003 | 17-Nov-05 | 71.0 | 3.8 |
| 48 | RM0204-044 | 02-Aug-05 | –1.980 | 0.004 | 17-Nov-05 | 73.3 | 4.1 |
| 49 | RM0204-176 | 03-Aug-05 | –1.992 | 0.002 | 17-Nov-05 | 71.2 | 4.0 |
| 50 | RM0204-053 | 17-Aug-05 | –1.987 | 0.003 | 16-Jan-06 | 75.5 | 3.9 |
| 51 | RM0204-097 | 22-Sep-05 | –1.983 | 0.002 | 23-Jan-06 | 75.0 | 4.0 |
| 52 | RM0204-160 | 05-Oct-05 | –1.972 | 0.004 | 24-Feb-06 | 63.7 | 4.2 |
| 53 | RM0204-034 | 05-Dec-05 | –1.996 | 0.002 | 14-Mar-06 | 75.9 | 3.9 |
| 54 | RM0204-141 | 07-Dec-05 | –2.004 | 0.003 | 14-Mar-06 | 74.2 | 3.9 |
| 55 | RM0204-188 | 19-Dec-05 | –1.953 | 0.005 | 24-Mar-06 | 62.4 | 3.9 |
| 56 | RM0204-083 | 20-Dec-05 | –1.977 | 0.005 | 24-Mar-06 | 67.0 | 3.8 |
| 57 | RM0204-010 | 26-Dec-05 | –1.949 | 0.005 | 24-Mar-06 | 76.7 | 4.1 |
| 58 | RM0204-173 | 30-Jan-06 | –2.015 | 0.003 | 23-May-06 | 59.0 | 3.8 |
| 59 | RM0204-001 | 01-Feb-06 | –1.949 | 0.006 | 23-May-06 | 57.3 | 4.0 |
| 60 | RM0204-172 | 02-Feb-06 | –1.940 | 0.003 | 26-May-06 | 62.1 | 3.6 |

Table 3.10.7. continued.

| No. | RS No. | $\delta^{13}C$ / ‰ | | | $\Delta^{14}C^{a}$ / ‰ | | |
|---|---|---|---|---|---|---|---|
| | | Measurement date | $\delta^{13}C$ | Error[b] | Measurement date | $\Delta^{14}C$ | Error[c] |
| 61 | RM0204-144 | 20-Feb-06 | –1.979 | 0.001 | 26-May-06 | 56.0 | 4.6 |
| 62 | RM0204-080 | 23-Feb-06 | –1.949 | 0.006 | 05-Jun-06 | 71.4 | 3.9 |
| 63 | RM0204-146 | 27-Mar-06 | –1.981 | 0.003 | 05-Jun-06 | 68.6 | 3.8 |
| 64 | RM0204-126 | 28-Mar-06 | –1.957 | 0.005 | 29-Jun-06 | 63.1 | 3.6 |
| 65 | RM0204-021 | 30-Mar-06 | –1.951 | 0.003 | 29-Jun-06 | 72.3 | 3.4 |
| 66 | RM0204-039 | 06-Jun-06 | –1.973 | 0.002 | 29-Jun-06 | 72.3 | 3.8 |
| 67 | RM0204-105 | 07-Jun-06 | –1.937 | 0.003 | 29-Jun-06 | 60.8 | 5.6 |
| 68 | RM0204-178 | 10-Jan-06 | –1.992 | 0.004 | 25-Jul-06 | 64.4 | 3.8 |
| 69 | RM0204-029 | 20-Feb-06 | –1.995 | 0.004 | 02-Aug-06 | 72.0 | 3.5 |
| 70 | RM0204-167 | 20-Mar-06 | –2.002 | 0.003 | 02-Aug-06 | 64.3 | 3.7 |
| 71 | RM0204-117 | 20-Mar-06 | –1.965 | 0.001 | 06-Oct-06 | 63.2 | 3.6 |
| 72 | RM0204-024 | 27-Mar-06 | –1.961 | 0.006 | 06-Oct-06 | 74.2 | 3.7 |
| 73 | RM0204-067 | 22-Jun-06 | –1.954 | 0.003 | 13-Oct-06 | 57.6 | 3.7 |
| 74 | RM0204-107 | 26-Jun-06 | –1.977 | 0.003 | 13-Oct-06 | 63.9 | 3.5 |
| 75 | RM0204-153 | 28-Jun-06 | –2.023 | 0.004 | 27-Oct-06 | 71.6 | 3.5 |
| 76 | RM0204-051 | 30-Jun-06 | –1.995 | 0.004 | 27-Oct-06 | 55.9 | 3.5 |
| | | mean | –1.983 | | mean | 66.3 | |
| | | standard deviation | 0.027 | | standard deviation | 5.8 | |

a. Decay corrected for 01/May/2004.
b. Standard deviation of repeat measurements.
c. Larger of the standard deviation and the counting error.

**(9) Quality control flag assignment**

Quality flag values were assigned to all $\delta^{13}C$ and $\Delta^{14}C$ measurements using the code defined in Table 0.2 of WHP Office Report WHPO 91-1 Rev.2 section 4.5.2 (Joyce et al., 1994). Measurement flags of 2, 3, 4, 5, and 6 have been assigned (Table 3.10.8). For the choice between 2 (good), 3 (questionable) or 4 (bad), we basically followed a flagging procedure in Key et al. (1996) as listed below:

a. On a station-by-station basis, a datum was plotted against pressure. Any points not lying on a generally smooth trend were noted.

b. $\delta^{13}C$ ($\Delta^{14}C$) was then plotted against dissolved oxygen (silicate) concentration and deviant points noted. If a datum deviated from both the depth and oxygen (silicate) plots, it was flagged 3.

c. Vertical sections against depth were prepared using the Ocean Data View (Schlitzer, 2006). If a datum was anomalous on the section plots, datum flag was degraded from 2 to 3, or from 3 to 4.

Table 3.10.8. Summary of assigned quality control flags.

| Flag | Definition | Number | |
|---|---|---|---|
| | | $\delta^{13}C$ | $\Delta^{14}C$ |
| 2 | Good | 2,486 | 2,518 |
| 3 | Questionable | 94 | 80 |
| 4 | Bad | 19 | 3 |
| 5 | Not report (missing) | 11 | 12 |
| 6 | Replicate | 217 | 214 |
| Total | | 2,827 | 2,827 |

**(10) Data Summary**

Figure 3.10.3 and 3.10.4 show vertical sections of $\delta^{13}C$ and $\Delta^{14}C$ against depth, respectively. Maximum of $\delta^{13}C$ was observed in the mode waters (SAMW: Subantarctic Mode Water) in the Pacific and Indian Oceans. In the Southwest Pacific Basin (180° - 130°W), Madagascan Basin (50°E - 60°E), and West Australian Basin (90°E - 110°E), high $\delta^{13}C$ waters near bottom well correspond to the Circumpolar Deep Water (CDW). In the South Atlantic Ocean, one can distinguish low-$\delta^{13}C$ water of the Antarctic Bottom Water (AABW) from high-$\delta^{13}C$ water of the North Atlantic Deep Water (NADW). Low $\delta^{13}C$ was found in deep waters in the Indian Ocean (IDW: Indian Deep Water) and in the Pacific Ocean (PDW: Pacific Deep Water) from 1,000 to 4,000 m depth approximately. The global distribution of $\delta^{13}C$ well agree with that presented in a previous study (Kroopnick, 1985). Temporal increase of the anthropogenic $CO_2$ inventory can be estimated by comparison the BEAGLE2003 $\delta^{13}C$ with historical data because atmospheric $\delta^{13}C$ decrease, named "$^{13}C$-Suess Effect", has been imprinted in $\delta^{13}C$ of DIC in surface ocean.

Higher $\Delta^{14}C$ values were observed in the thermocline (< about 1,000 m depth) of the three basins because of the bomb-produced radiocarbon penetration. Deep $\Delta^{14}C$ data clearly indicate the global pattern of thermohaline circulation. Relative higher $\Delta^{14}C$ was measured in CDW where the high-$\delta^{13}C$ water was found. In the South Atlantic Ocean, one can distinguish low-$\Delta^{14}C$ water of AABW from high-$\Delta^{14}C$ water of NADW. Minimum of $\Delta^{14}C$ was measured in IDW and PDW where the $\delta^{13}C$ minimum was found. The global distribution of $\Delta^{14}C$ in deep and bottom waters supports a previous study (Key et al., 2004). Difference between BEAGLE2003 and historical radiocarbon data will suggest temporal change of bomb radiocarbon in the thermocline.

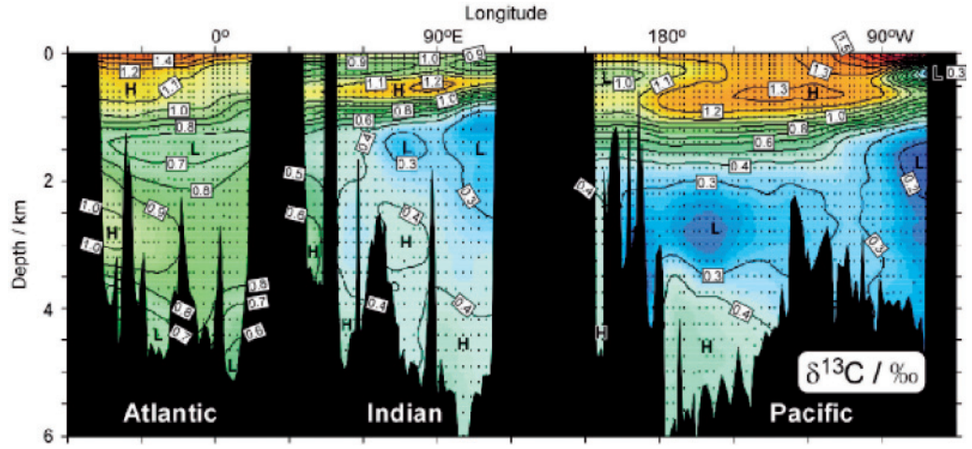


Figure 3.10.3. Vertical sections of $\delta^{13}C$ against depth during BEAGLE2003 cruise in 2003/2004.

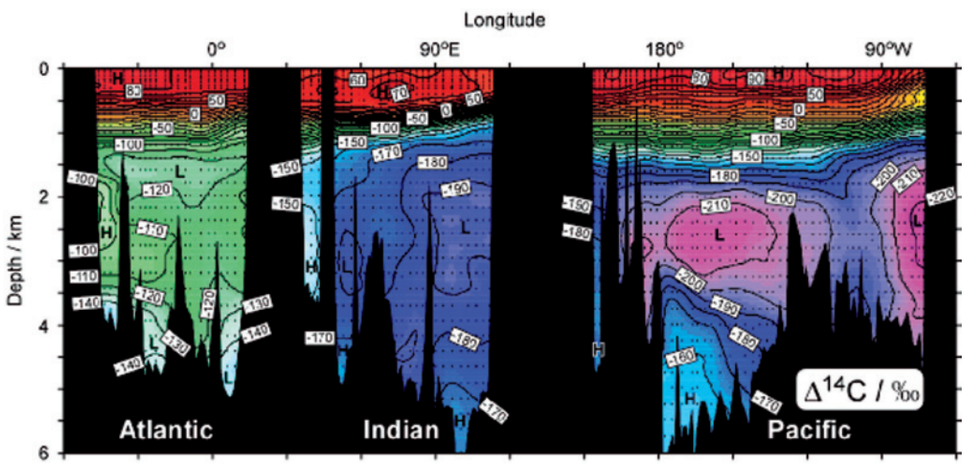


Figure 3.10.4. Vertical sections of $\Delta^{14}C$ against depth during BEAGLE2003 cruise in 2003/2004.

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## 3.11 Anthropogenic radionuclides

*23 January 2007*

### 3.11.1 General information

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A. Takeuchi: The General Environmental Technos Co., LTD (KANSO)

S. Lee: International Atomic Energy Agency, Marine Environmental Laboratories (IAEA-MEL)

B. Oregioni: IAEA-MEL

J. Gasutaud: IAEA-MEL

**(2) Objectives**

1) Geochemical studies of global fallout, anthropogenic radionuclides such as $^{137}$Cs, $^{90}$Sr and Pu isotopes, including studies on the long term behaviour of $^{137}$Cs in the world ocean, and to learn more about the present geographical distribution of $^{137}$Cs in the oceans in the southern hemisphere.
2) Use of anthropogenic radionuclides as tracers for oceanographic and climate change studies. Development of the anthropogenic radionuclides database for validation and update of ocean general circulation models.

**(3) Target radionuclides**

Main target radionuclides are $^{137}$Cs, Pu isotopes and tritium. In some samples analysis of $^{90}$Sr will be carried out as well.

**(4) Sampling procedures**

Seawater sampling for analysis of radionuclides in the water column was carried out using adopted procedures. If additional Niskin bottles filled with samples were available, volumes of water column samples varied from 6 L to 20 L. The samples were drawn from Niskin bottles into 20 L cubitainers. The samples were then filtered through 0.45 $\mu$m pore size filters and filled into cubitainers or bottles of appropriate sizes. Filters were also archived. Concentrated nitric acid was added to the samples to keep pH at 1.6, except for tritium samples.

Surface water samples were drawn through an intake pump located several meters below the sea surface. Volumes up to 85 L were collected for $^{137}$Cs and Pu analysis. For tritium analysis, samples of 1 L were collected.

All samples were stored in a storage room at a stable temperature by the end of the cruise. In March 2004 the samples were loaded on land and transported to MRI at Tsukuba for the analysis of radionuclides on land. In June 2004, selected samples were sent to IAEA-MEL at Monaco for the analysis of radionuclides on land, too.

**(5) Samples accomplished during the cruises**

A total of 91 samples were collected for surface seawater samples. At the 56 stations, a total of 777 samples were collected for water column samples (Table 3.11.1). The sampling locations and depths are shown in Figure 3.11.1. A total weight of the samples was around 22,000 kg.

Table 3.11.1. Number of stations for each ocean.

| | The Pacific Ocean | The Atlantic Ocean | The Indian Ocean | Total |
|---|---|---|---|---|
| Surface | 51 | 18 | 22 | 91 |
| Water column | 27 | 12 | 17 | 56 |

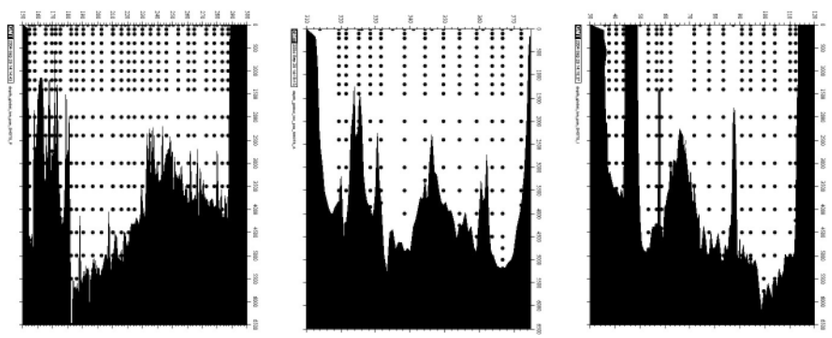

Figure 3.11.1. locations and depths of sampling sites.

**(6) Problems during the cruise and solutions**

No serious problems occurred during the cruise.

**(7) Comparability on the analysis of radionuclides among the laboratories on land**

Since the samples were measured by several laboratories on land, we checked the comparability of the measurements. Results are presented in Table 3.11.2, 3.11.3 and 3.11.4.

Table 3.11.2. Results of intercomparison of $^{137}$Cs measurements.

| | MRI (Bq m$^{-3}$) | MEL (Bq m$^{-3}$) | LLRL (Bq m$^{-3}$) | Comenius Univ. (Bq m$^{-3}$) |
|---|---|---|---|---|
| P06C-127 | 1.23±0.00 | 1.24±0.06 | | |
| | 1.20±0.04 | | | |
| I03-507 | 1.36±0.07 | | | 1.32±0.07 |
| | 1.19±0.05 | | | |
| A10-X15 | 1.23±0.06 | 1.15±0.03 | | |
| | 1.20±0.04 | | | |
| 165E-33-800 | 0.97±0.03 | | 1.14±0.05 | |
| 165E-33-900 | 0.63±0.02 | | 0.78±0.04 | |
| 165E-33-1000 | 0.50±0.05 | | 0.66±0.06 | |
| 165E-37-800 | 0.55±0.03 | | 0.69±0.05 | |

Table 3.11.3. Results of measurements of $^{137}$Cs in IAEA-381 reference material (Irish seawater).

| | MRI (Bq kg$^{-1}$) | MEL (Bq kg$^{-1}$) | Certified value (Bq kg$^{-1}$) |
|---|---|---|---|
| IAEA381 | 0.445±0.002 | | 0.49±0.01 |

Table 3.11.4. Results of intercomparison of Pu measurements.

| | MRI (mBq m$^{-3}$) | MEL (mBq m$^{-3}$) | KINS (mBq m$^{-3}$) |
|---|---|---|---|
| P06C-175 | 1.1±0.3 | | 1.41±0.24 |
| P06C-124 | 1.5±0.4 | | |
| P06C-127 | | | |

## 3.11.2 Analyses at Meteorological Research Institute (MRI) and Low Level Radioactivity Laboratory , Kanazawa University (LLRL) in Japan

M. Aoyama (MRI), K. Hirose (MRI, LLRL), K. Komura (LLRL), and Y. Hamajima (LLRL)

**(1) Personnel**

M. Aoyama: MRI

K. Hirose: MRI, Low Level Radioactivity Laboratory, Kanazawa University (LLRL)

K. Komura: LLRL

Y. Hamajima: LLRL

**(2) Analytical method of $^{137}$Cs analysis in seawater at MRI and LLRL**

Cs is one of the alkali metals, which exists in ionic form in natural water, and chemically shows less affinity than other chemicals. Known adsorbents to collect Cs in seawater are ammonium phosphomolybdate (AMP) and hexacyanoferrate compounds (Folsom and Sreekumaran, 1966; La Rosa et al., 2001). The AMP has been an effective ion exchanger of alkali metals (Van R. Smit et al., 1959). Aoyama et al. (2000) re-examined the AMP procedure and their experiments revealed that the stable Cs carrier of the same equivalent amount as AMP is required to form insoluble Cs-AMP compounds in an acidic solution (pH from 1.2 to 2.2). The improved method has achieved high chemical yields of more than 95 % for sample volumes of less than 100 L. Another improvement is a reduction of the amount of AMP from ~10 g to 4 g to adsorb $^{137}$Cs from seawater samples. As a result, it has been possible to reduce the sample volumes from ~100 L to less than 20 L, so after final sample treatment high-efficiency well-type Ge-detectors can be used for analysis of $^{137}$Cs. These improvements have enabled to apply $^{137}$Cs as a chemical tracer for studying oceanographic processes in much larger scales, as has been documented during the BEAGLE cruise.

Recently Komura (Komura, 2004; Komura and Hamajima, 2004) has established an underground facility (Ogoya Underground Laboratory, OUL) to achieve an extremely low background of γ-spectrometers, operating with Ge detectors of high efficiency. The OUL has been constructed in 1995 by Low Level Radioactivity Laboratory of the Kanazawa University in the tunnel of former Ogoya copper mine (235 m above the sea level, Ishikawa prefecture). The shielding depth of the OUL is 270 m of water equivalent, where contributions of meaon are more than four orders of magnitude lower than at the ground level. In order to achieve an extremely low background of γ-spectrometers, high efficiency well type Ge detectors specially designed for low level γ-ray spectrometry were shielded with low background lead prepared from old roof tiles of the Kanazawa Castle. As a result, the background of γ-ray spectrometers in the energy range of $^{137}$Cs is two orders of magnitude lower than that in ground-level facilities, as shown in Table 3.11.5. A detection limit of $^{137}$Cs at the OUL is 0.18 mBq for a counting time of 10000 minutes (Hirose et al., 2005).

There is a residual problem in low-level γ-spectrometry for $^{137}$Cs measurements as AMP adsorbs trace amounts of potassium when Cs is extracted from seawater. Potassium is a major component in seawater, and natural potassium compounds contains 0.0118 % of radioactive potassium ($^{40}$K) to stable potassium. Therefore even trace amounts of $^{40}$K cause elevation of background in the $^{137}$Cs energy window due to Compton scattering of gamma-rays from $^{40}$K. If $^{40}$K can be removed from AMP(Cs) compound samples, a better sensitivity of underground γ-spectrometers for $^{137}$Cs measurements can be achieved. To remove $^{40}$K from AMP(Cs) compounds, a precipitation method including insoluble platinate salt of Cs was developed for purification of Cs. This method helped to remove trace amounts of $^{40}$K from from AMP(Cs) compounds with a chemical yield of around 90 % for $^{137}$Cs (Hirose et al., 2007).This metod has been applied for seawater samples collected below the 1200 m water depth.

*Materials and procedures of chemical separation*

All reagents used for $^{137}$Cs, $^{90}$Sr and Pu assay are special (G.R.) grade for analytical use. All experiments and sample treatments have been carried out at ambient temperatures. It is very important to know background γ-activity of reagents. The $^{137}$Cs activity of CsCl and AMP reagents was less than 0.03 mBq g$^{-1}$ and 0.008 mBq g$^{-1}$, respectively. There has not been any $^{137}$Cs contamination observed from other reagents.

An improved AMP procedure of chemical separation of $^{137}Cs$ from seawater samples for the ground-level γ-spectrometry was as follows:

1) Measure the seawater volume (5-100 L) and put the sample into a tank of appropriate size.
2) pH should be adjusted to be 1.6-2.0 by adding concentrated $HNO_3$ (addition of 40 mL conc. $HNO_3$ for 20 L seawater sample makes pH of seawater sample about 1.6).
3) Add CsCl of 0.26 g to form an insoluble compound, and stir at a rate of 25 L per minute for several minutes.
4) Weigh AMP of 4 g and pour it into a tank to disperse the AMP with seawater.
5) 1 hour stirring at the rate of 25 L air per minute.
6) Settle until the supernate becomes clear. A settling time is usually 6 hours to overnight, but no longer than 24 hours.
7) Take an aliquot of 50 mL supernate to calculate the amount of the residual caesium in the supernate.
8) Loosen the AMP(Cs) compound from the bottom of the tank and transfer into a 1-2 L beaker, if it is necessary do an additional step of decantation.
9) Collect the AMP/Cs compound onto 5 B filter by filtration and wash the compound with 1 M $HNO_3$
10) Dry up the AMP(Cs) compound for several days in room temperature
11) Weigh the AMP(Cs) compound and determine weight yield
12) Transfer the AMP(Cs) compound into a teflon tube of 4 mL volume and analyze in a γ-ray spectrometer.

$^{137}Cs$ measurements were carried out by γ-spectrometry using well-type Ge detectors coupled with multi-channel pulse height analyzers. The performance of the well-type Ge detectors is summarized in Table 3.11.5. The detector energy calibration was done using IPL mixed γ-ray sources, while the geometry calibration was done using an internal reference material of similar density, placed in the same sample tube.

Table 3.11.5. The performance of HPGe coaxial well-type detectors (Hirose et al., 2007).

| Institute | Type | Active volume ($cm^3$) | Absolute efficiency[a] (%) | Background[b] (cpm/1keV) |
|---|---|---|---|---|
| MRI | ORTEC 6 | 280 | 20.5 | 0.092 |
| | 7 | 80 | 10.8 | 0.033 |
| | 8 | 280 | 16.5 | 0.109 |
| | 9 | 600 | 23.7 | 0.074 |
| Ogoya | Canberra | 199 | 14.5 | 0.0005 |
| | EYRISYS | 315 | 20 | 0.0016 |

a: The absolute efficiencies of HPGE are calculated at 662 keV photo-peak of $^{137}Cs$.

b: The background values were calculated as a sum from 660 keV to 664 keV corresponding to 662 keV photo-peak of $^{137}Cs$.

For samples collected deeper than 1200 m, an additional treatment using $Cs_2Pt(Cl)_6$ precipitate was applied to remove traces of $^{40}K$. These samples were analyzed for $^{137}Cs$ in the underground facility at Ogoya.

1) the same procedure from step 1) to step 12).
2) Dissolve the AMP(Cs) compound by adding alkali solution.
3) pH should be adjusted to 8.1 by adding 2 M HCl and adjust the volume of solution to 70-100 mL.
4) Perform precipitation of $Cs_2Pt(Cl)_6$ adding chloroplatinic acid (1g/5mL DW) at pH = 8.1 and keep in refrigerator during a half-day.
5) Collect the $Cs_2Pt(Cl)_6$ precipitate onto a filter by filtration and wash the compound with solution (pH = 8.1).
10) Dry up the $Cs_2Pt(Cl)_6$ precipitate for several days at room temperature.
11) Weigh the $Cs_2Pt(Cl)_6$ precipitate and determine weight yield.

12) Transfer the $Cs_2Pt(Cl)_6$ precipitate into a teflon tube of 4 mL volume and analyze by underground γ-spectrometry.

**(3) Analytical method of $^{239+240}$Pu in seawater at MRI**

*Preconcentration of Pu*

Co-precipitation method of Pu with Fe hydroxides was used as a preconcentration method. Seawater sample of 60 L was acidified to pH=2 with 12 M HCl (60 mL). After addition of ferric chloride (0.6 g), a known amount of tracer ($^{242}$Pu) and $K_2S_2O_5$ (30 g), the solution was stirred for 1 h. In this stage, all Pu species in solution were reduced to Pu(III). Coprecipitation of Pu with ferric hydroxide was formed at pH=10 to adding dilute NaOH solution (0.5-1 M). The formed ferric oxide precipitation contained small amounts of $Ca(OH)_2$ and $Mg(OH)_2$.

*Radiochemical separation*

Precipitates (Fe, Mg, Ca hydroxides) were dissolved with 12 M HCl and added to bring the acid strength to 9 M (three times of the dissolved materials). One drop of 30 % $H_2O_2$ was added for each 10 mL solution, and the solution was heated just below boiling for 1 h. After the solution had cooled, Pu was isolated by anion exchange techniques (Dowex 1-X2 resin, 100 mesh; a large column (15 mm of diameter and 250 mm long) was used.) The sample solution passed through the column and was washed with 50 ml 9 M HCl. In this stage, Pu, Fe and U were retained onto resin, whereas Am and Th were in effluents. Fe and U fractions were sequentially eluted with 8 M $HNO_3$. After elution of U, the column was washed with 5 ml 1.2 M HCl. Finally Pu fraction was eluted with 1.2 M HCl (100 ml) containing 2 ml of 30% $H_2O_2$. The solution was dried onto hot plate. The chemical yield was around 70 %.

*Electrodeposition*

Pu samples for α-spectrometry were electroplated onto stainless steel disks. The diameter of stainless steel disk depends on the active surface area of detectors. The electrodeposition was performed using an electrolysis apparatus with electrodeposition cell consisting of teflon cylinder, a cathode of platinum electrode and an anode of stainless steel disk.

The purified Pu fraction was dissolved in 1 mL of 2 M HCl and transferred into an electrodeposition cell using 20 mL ethanol. Pu was then electroplated onto a stainless steel disk (30 mm in diameter) at 15 V and 250 mA for 2 hours.

*α-spectrometry*

The α-spectrometers consist of several vacuum chambers with solid-state detectors, a pulse height analyzer and a computer system. The detector, which is silicone surface barrier type (PIPS, energy resolution: <25 keV (FWHM), counting efficiency: 15 - 25 %), has an active surface area of 450 - 600 mm$^2$ and a minimum depletion thickness of 100 $\mu$m. The vacuum in the chamber is less than 100 mTorr by using a vacuum pump. The counting time was more than 800000 s. Counting uncertainties (1σ) for BEAGLE samples were 10 - 20 %.

### 3.11.3 Analyses at Marine Environmental Laboratories (IAEA-MEL) in Monaco, Comenius University of Bratislava in Slovakia, and Risoe National Laboratory (RNL) in Denmark

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**(1) Personnel**

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P. P. Povinec: Comenius University of Bratislava

P. Ross: Risoe National Laboratory (RNL)

J. Gastaud: IAEA-MEL

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I. Levy-Palomo: IAEA-MEL

S. Rezzoug: IAEA-MEL

I. Sykora: Comenius University of Bratislava

**(2) Introduction**

IAEA-MEL performed the radiochemical separation of samples from the Atlantic and Indian Oceans. The seawater samples were filtered (0.45 $\mu$m) and acidified on board RV Mirai and sent to Monaco. In average, the volumes received were 80 L for surface and 20 L for deeper samples. For all samples, plutonium and caesium were analyzed. Strontium was analyzed all surface samples and 4 profiles. Therefore, 3 separation processes were sequentially performed based on co-precipitation techniques. Also, selected samples were analyzed for tritium.

**(3) Sample preparation**

When transferring the acidified filtered sea water samples to the precipitation containers, sample volume and weight were determined. After adjusting pH to1, plutonium tracer ($^{242}$Pu: 1,022 dpm per sample) and carriers (caesium: 40 to 800 mg, depending on sample volume; strontium: 1 g) were added.

*Pre-concentration of plutonium with manganese dioxide*

After mixing of the tracer and the carriers to equilibrium, saturated $KMnO_4$ (0.5 mL per liter of sample) was added to the samples and stirred. To precipitate $MnO_2$, 0.5 M $MnCl_2$ (1 mL per liter of sample) was added to the sample and pH was increased to 9 with 10M NaOH. After precipitation and stirring, the pH was readjusted to 8. The precipitate was allowed to settle overnight. The supernatant was carefully siphoned and transferred to another container for the caesium separation. The $MnO_2$ (Pu) precipitate was poured into a beaker for further chemical separation.

*Pre-concentration of caesium with ammonium molybdophosphate (AMP)*

The supernatant solution was re-acidified to pH 1.5 - 2 with concentrated HCl (1 to 1.5 mL per liter of sample). Addition of a few ml of 30 % $H_2O_2$ was needed to dissolve a small amount of $MnO_2$ suspension carried over from the previous step. A slurry of AMP (0.2 g per liter of sample) in water was added and the suspension stirred for 30 minutes. The AMP was let to settle in the tank. For the subsequent precipitation of Ca(Sr) oxalate, the samples were transferred to another container. The AMP(Cs) precipitate was poured into a beaker for further chemical processing.

*Pre-concentration of strontium with calcium oxalate*

The strontium is co-precipitated with calcium as an insoluble oxalate from solution containing excess oxalic acid and adjusted to pH 5 - 6. As the Sr chemical recovery is estimated by X-Ray fluorescence, an aliquot of the seawater was collected kept before the Ca(Sr) precipitation. The mixed Ca(Sr) oxalate precipitation was carried out by adding an appropriate quantity of oxalic acid dissolved in very hot de-ionized water (10g per liter of sample) to the AMP(Cs) supernatant solution, mixing well and adjusting to a final pH 5 - 6 with 10M NaOH. The Ca(Sr) oxalate precipitate was let to settle overnight. Afterwards, the supernate was pumped out. The Ca(Sr) mixed oxalate precipitate was recovered from the tank bottom and transferred into a beaker for further separation.

The schematic diagram of pre-concentration of radionuclides in seawater is shown in Figure 3.11.2.

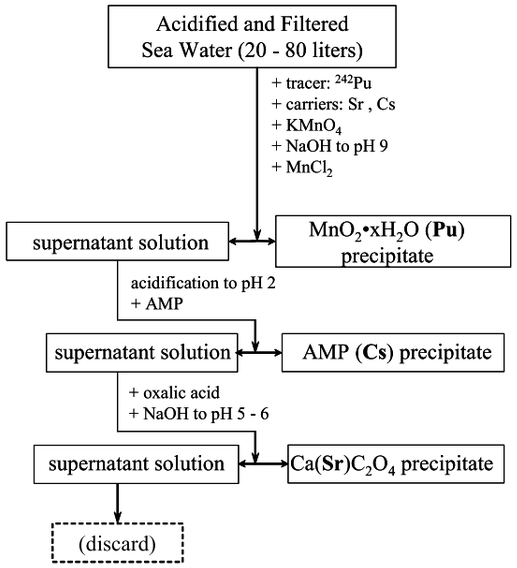


Figure 3.11.2. Pre-concentration of radionuclides in sea water.

**(4) Plutonium analysis**

*Dissolution of manganese dioxide*

After the precipitate settled in the beaker, the supernatant was siphoned out. The solution containing the $MnO_2$ precipitate was acidified to pH 1 and a solution of hydroxylammonium hydrochloride ($NH_2OH•HCl$, 0.1 g/ml) was added in small portions to the hot suspension until all of the manganese dioxide had dissolved by reduction from Mn(IV) dioxide to soluble Mn(II).

*Oxidation state adjustment of plutonium*

Fifty milligrams of Fe(III) were added. A few mL of $NH_2OH•HCl$ solution were added and the manganese-iron-Pu solution was heated to reduce Fe(III) to Fe(II). The Fe(II) rapidly reduced all soluble Pu species to Pu(III). After the reduction to Fe(II) and Pu(III), 2 g of $NaNO_2$ dissolved in 20 mL of water was added to the hot solution in order to oxidize the excess $NH_2OH•HCl$ and to convert Fe(II) and Pu(III) to Fe(III) and Pu(IV), respectively.

*Iron hydroxide precipitation*

$NH_4OH$ was added to the hot solution to make the pH 8 - 9, causing precipitation of $Fe(OH)_3$ and co-precipitation of Pu(IV). The freshly precipitated iron hydroxide was flocculated by heating. After heating, the pH of the suspension was adjusted to 6 - 7 with HCl. At this pH, manganese will stay in solution but the flocculated iron hydroxide and its co-precipitated Pu(IV) remain insoluble.

The iron hydroxide (Pu) was left to settle overnight. The $Fe(OH)_3$ (Pu) was separated from the supernatant solution by siphoning and the precipitate was separated by centrifugation of the suspension left in the precipitating vessel. Hot, concentrated HCl was used to dissolve the separated iron hydroxide, including that on the wall of the precipitating beaker. Concentrated nitric acid additions and evaporations were used to convert this to a nitrate salt residue. (Figure 3.11.3)

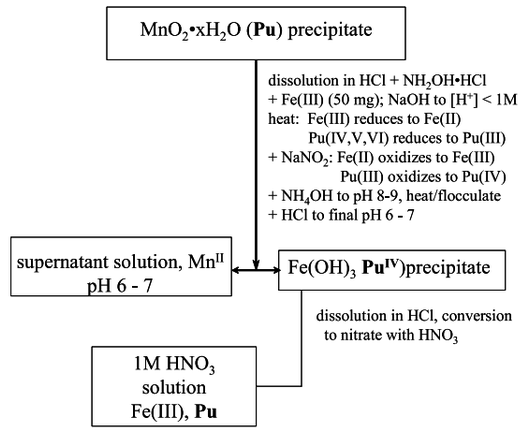


Figure 3.11.3. Dissolution and treatment of $MnO_2•xH_2O$ (Pu) concentrate.

*Preparations for Pu separation by anion exchange*

The Fe(Pu) precipitate was dissolved in 1 M $HNO_3$ and after adding hydrazinium hydrate (1 to 2 mL). The solution was heated to facilitate the reduction of Fe(III) to Fe(II). Successful conversion of the iron to the ferrous state ensures that the dissolved Pu species are brought to their lower oxidation states of III and IV. Excess $N_2H_4 \bullet H_2O$ was destroyed by adding 70 % $HNO_3$ and heating the solution strongly. At this stage, Pu was in the Pu(IV) oxidation state, but this was further assured by adding $NaNO_2$ to the cooled solution and boiled. Finally, the solution was adjusted to 7 - 8 M $HNO_3$ with 70 % $HNO_3$.

*Plutonium separation by column chromatography*

The anion exchange resin used was analytical grade AG 1-X8, 100 - 200 mesh bead size, supplied in the chloride form from Bio-Rad. A water slurry of the resin (10 mL) was loaded into a 30 cm glass column (1 cm inner diameter). The resin was conditioned from chloride to nitrate form by passing 8 M $HNO_3$ (50 mL) through the resin bed.

The sample solution (7 - 8 M $HNO_3$) from the previous step and the rinse solution of the beaker were loaded into the column reservoir. This was followed by 50 ml of 8 M $HNO_3$ “wash” to rinse the feed solution thoroughly out of the column (removing non-retained species such as Am, Fe, Al, Ca, K). After this wash, 100 mL of 10 M HCl were passed through the column to elute thorium. The plutonium was eluted with freshly prepared 0.1 M $NH_4I$-9M HCl. The so-called “Pu strip” was collected in a beaker. This solution was evaporated down. Iodine was removed as volatile iodine ($I_2$) vapour by repeated additions of concentrated $HNO_3$ with small portions of 30 % $H_2O_2$. (Figure 3.11.4)

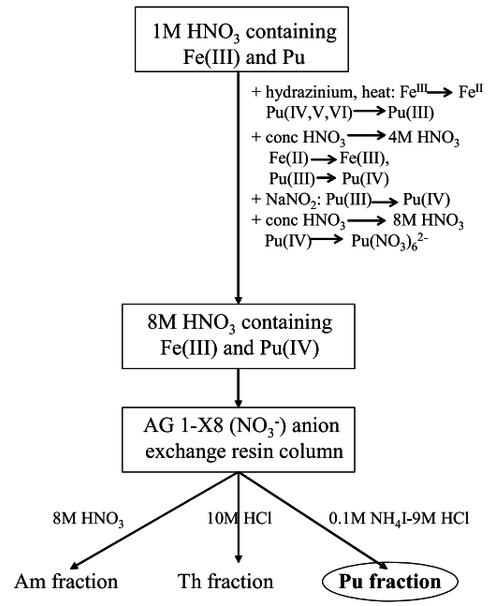


Figure 3.11.4. Separation of Plutonium by oxidation state adjustment and anion exchange chromatography.

*Neodynium fluoride precipitate*

Considering that Pu was to be measured by ICP-MS, it is important to efficiently remove the uranium with $NdF_3$ precipitations. The solution residue (Pu) was dissolved in 1 M $HNO_3$ and transferred to a centrifuge tube with the rinsing solution of the beaker. 10 mg of Nd (from a neodymium oxide solution) was added and a sequence of reduction-oxidation of the Pu was done by adding Mohr’s salts followed by 25 % $NaNO_2$ solution. The Pu was co-precipitated as $NdF_3$ by adding concentrated HF (5 ml). This precipitate was centrifuged to remove the supernatant. The dissolution of the precipitate was done with 4 M $HNO_3$-$H_3BO_3$ (10 mg/ml). A second precipitation was carried out in the same conditions. Finally, after dissolution, the precipitate was conditioned in 3 M $HNO_3$. (Figure 3.11.5)

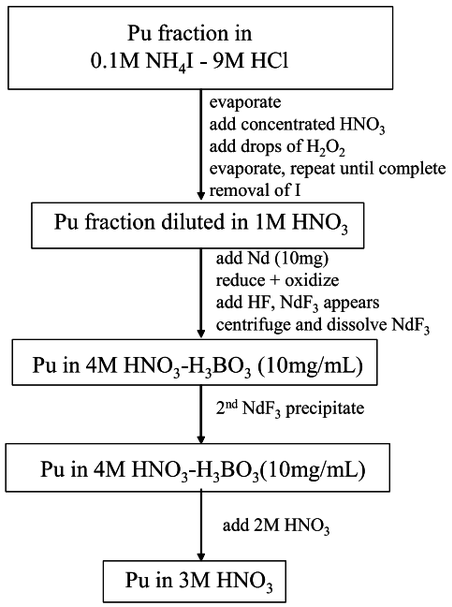


Figure 3.11.5. Separation of Plutonium by $NdF_3$ precipitation.

*Plutonium separation by Eichrom-TEVA column*

The purpose is to separate thorium traces in the solution. The pre-packed TEVA column (2 mL) was conditioned in 3 M $HNO_3$ and the solution was passed through it. The rinsing and following cleaning steps were processed with Ultra-Pure (UP) acids. First, thorium was eluted with 10 M HCL UP. Then Pu was eluted with a 0.1 M HCl-0.1 M HF UP solution in a Teflon beaker. (Figure 3.11.6)

*Preparation of samples for ICP-MS measurements*

The final solution was evaporated to dryness, treated a few times with concentrated $HNO_3$ UP and dried. The residue was diluted and the walls of the beaker were rinsed with 1 M $HNO_3$ UP. The 3 successively small volumes (0.5 mL, 0.5 mL and 0.25 mL) used were transferred to closed plastic tubes for further analysis by ICP-MS.

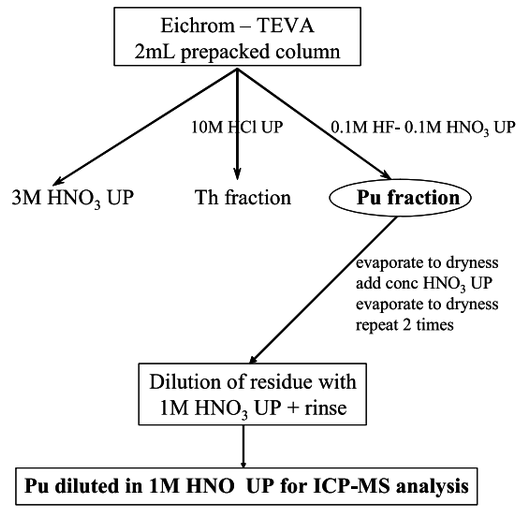


Figure 3.11.6. Plutonium separation by Eichrom-TEVA column and preparation for ICP-MS analysis.

*ICP-MS analysis*

Samples were analyzed using a high resolution ICP-MS at Risoe National Laboratory. An ultrasonic nebuliser was used for introduction of samples into the spectrometer. The settings of the system were as follow:

Xs- cones with Cetac USN 5000+. Heater 140 °C, cooler 3 °C

Extraction voltage –694 V

Lens 1 –1019 V

Lens 2 –69 V

Auxiliary gas 0.7 lpm

Nebuliser gas 0.92 lpm

RF power 1405 W

Hexapole bias –2 V

Sample uptake rate: 0.5 ml/min

Sensitivity $^{238}U$: 4.5 MHz/ppb

Number of points per peak: 1

Dwell time: 50 ms ($^{239\&240}Pu$), 1ms ($^{238}U$), 2ms ($^{242}Pu$)

Number of sweeps: 250

Repetitions per sample: 20

Reagent blanks and reference materials were analyzed together with the seawater samples. An example of the mass spectrum obtained is shown in Figure 3.11.7.

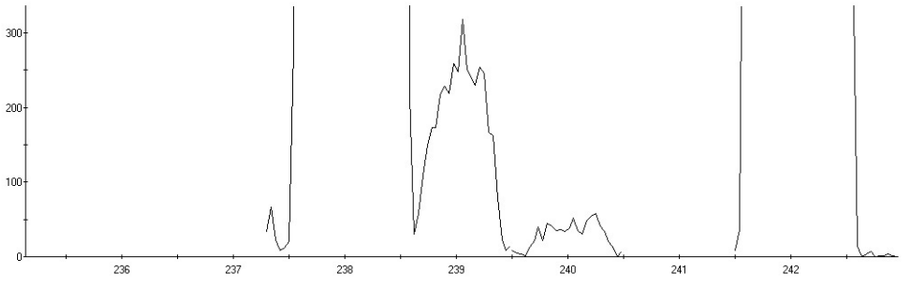


Figure 3.11.7. mass spectrum of plutonium solutions.

**(5) Caesium analysis**

AMP(Cs) was transferred into a beaker, decanted and the supernatant was siphoned. The AMP(Cs) was finally centrifuged. The separated AMP was dissolved in a minimum amount of 10 M NaOH. As some fine-particle suspension of $MnO_2$ was carried over in the supernatant solution from the first pre-concentration step ($MnO_2$ precipitation for Pu) and subsequently scavenged by the AMP, the insoluble fraction was separated by centrifugation. The AMP(Cs) solution in NaOH was transferred to a beaker, heated and boiled to drive off ammonia in order to minimize precipitation of AMP when the solution is re-acidified.

The boiled Cs-AMP-NaOH solution was cooled and diluted to about 500 mL with water. Concentrated HCl was added to adjust the solution to pH 2. Then, 1 g of fresh AMP was added and stirred to collect the Cs (2nd AMP-Cs precipitation). After settling and decantation, the 2nd AMP-Cs was separated by centrifugation and washed. It was again dissolved in a minimum amount of 10 M NaOH, and any eventual insoluble fraction was discarded by centrifugation. The solution was introduce into a standard geometry for gamma-ray counting. (Figure 3.11.8)

The recovery of this process was finally estimated by AAS from a small aliquot of the final solution.

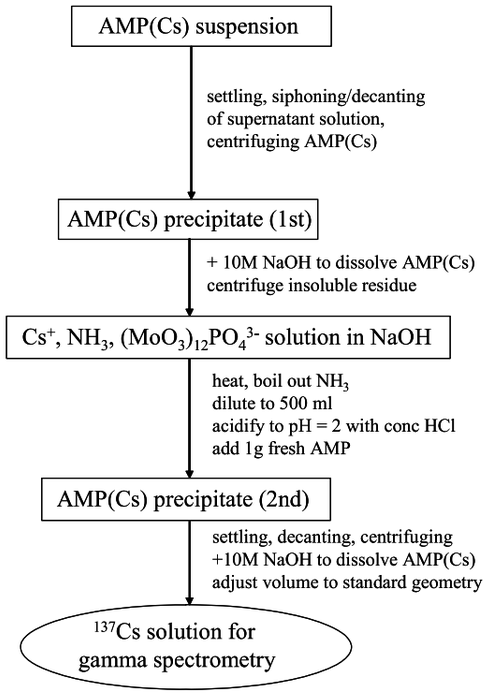


Figure 3.11.8. Caesium separation for gamma-spectrometry.

*Gamma-spectrometry at IAEA-MEL*

The AMP(Cs) samples were analyzed with high-purity well-type germanium detectors in the underground laboratory at IAEA-MEL. Ultra-low background is achieved by using very old lead and an anticosmic shield (Figure 3.11.9, Povinec et al., 2005). The detectors used had relative efficiencies ranging from 100 to 200 %, and $^{40}K$ background count rates ranging from 1 - 5 $10^{-4}$ $s^{-1}$. A typical spectrum from a sample taken at 1000 m water depth is shown in Figure 3.11.10.

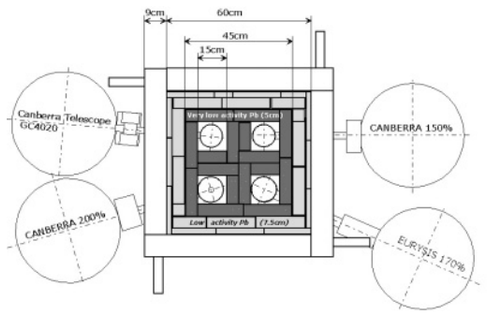


Figure 3.11.9. Schematic diagram of the IAEA-MEL underground (CAVE) facility (Povinec et al., 2005).

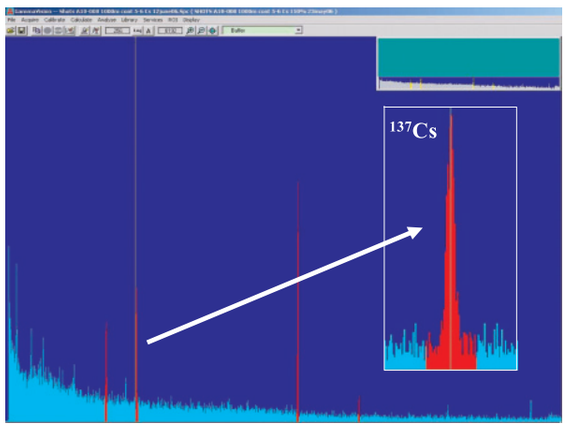


Figure 3.11.10. Gamma-ray spectrum of a sweater sample collected at 1000 m water depth in the Atlantic Ocean.

*$^{137}Cs$ gamma-ray spectrometry of seawater samples from the Indian Ocean carried out at the Comenius University of Bratislava, Slovakia*

Indian Ocean seawater samples prepared in IAEA-MEL as AMP(Cs) samples were analyzed in the Comenius University of Bratislava, Slovakia. Two shields for low background gamma-ray spectrometers located at about 10 m of water equivalent were built in the Department of Nuclear Physics of the Comenius University of Bratislava, Slovakia (Figure 3.11.11; Sykora et al., 1992; Sykora et al. 2006). The larger one has the outer dimensions of 2×1.5×1.5 m. It is composed of the following layers (from the outside to the inside): 10 cm of lead, 10 cm of electrolytic cooper, 10 cm of polyethylene with boric acid, 0.1 cm of electrolytic cooper, 0.1 cm of cadmium and 1cm of perspex. On the top, a layer of 12 cm of iron is added. The inner dimensions of the shield are 80×90×172 cm. To further reduce the detector background, and to decrease the radon contribution and stabilize its content in the shield (by flushing the detector chamber with nitrogen evaporated from a cooling Dewar), an extra copper shield (12×20×30 cm) has been inserted inside the large shield (Figure 3.11.11).

Figure 3.11.11. Small (left) and large (centre and right) shields for low-level gamma-ray spectrometry constructed in the Department of Nuclear Physics of the Comenius University of Bratislava, Slovakia.

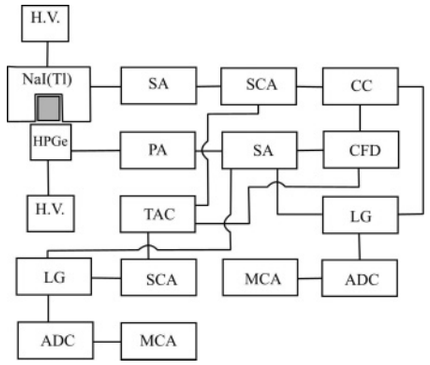


Figure 3.11.12. Schematic diagram of electronic circuits of the coincidence-anticoincidence spectrometer.

The copper has been used because of its low radioactive contamination by uranium and thorium and their decay products. A HPGe coaxial detector produced by PGT (USA) with 70 % relative efficiency (for 1332.5 keV and relative to 75×75 mm NaI(Tl) crystal) and of 270 $cm^3$ sensitive volume operates in this shield. The smaller shield (Figure 3.11.11) has a similar composition of layers to the large shield, however, its inner dimensions are 38×38×62 cm only.

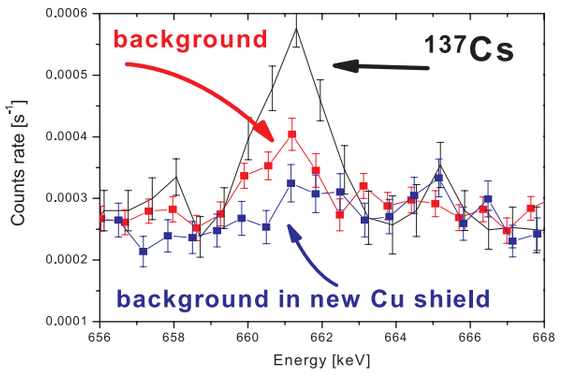


Figure 3.11.13. Comparison of background and sample counting rates in the old and in the additional Cu shield under the 661.6 keV peak of $^{137}Cs$.

A HPGe coaxial detector of 50 % relative efficiency produced by Canberra (USA), or a HPGe detector of 6 % relative efficiency with Be window produced by ORTEC (USA), operates in this shield. A block scheme of electronics used for coincidence-anticoincidence measurements, anti-Compton (with NaI(Tl) well detector) and/or with anti-cosmic shielding (with plastic scintillation detector) is schown in Figure 3.11.12. A background reduction in the $^{137}Cs$ window after introduction of the additional copper shield into the large shield is shown in Figure 3.11.13.

Typical applications have included non-destructive analysis of natural and anthropogenic radionuclides (mainly cosmogenic $^{7}Be$, radiogenic $^{210}Pb$ and anthropogenic $^{137}Cs$) in marine and terrestrial samples.

**(6) Strontium analysis**

*Strontium purification*

The calcium oxalate suspension was allowed to settle after transferring into a large beaker. The supernatant solution was siphoned off and the precipitate was centrifuged. It was then dried and ashed at 600 °C to convert the oxalate to carbonate. The ashed sample was weighed to determine the amount of 70 % $HNO_3$ to be added. A volume of 70 % $HNO_3$ in mL equal to seven times the ash weight in grams was slowly added to the calcium-strontium carbonate ash in an appropriate beaker. Strontium nitrate (1st) precipitates from this medium while the calcium remains in solution. Barium, radium and lead are expected to accompany the strontium nitrate.

The 1st strontium nitrate precipitate was separated from the mother solution containing the dissolved calcium-strontium ash by decanting the supernatant solution after settling. Heating the strontium nitrate suspension for some hours before allowing it to settle improves the separation by producing a $Sr(NO_3)_2$ precipitate of larger crystal size. This 1st $Sr(NO_3)_2$ precipitate was transferred to a pre-weighed 150 ml beaker, then washed with three 30 - 50 mL portions of acetone to remove $HNO_3$ and more soluble calcium nitrate. The washed $Sr(NO_3)_2$ was dried under a heat lamp and weighed. A volume of water in ml equal to 1.5 times the weight of dried precipitate in grams was added. This precipitate of $Sr(NO_3)_2$ will easily dissolve to give a clear solution.

After the salt was dissolved, a second $Sr(NO_3)_2$ precipitate was obtained by adding a volume of 70 % $HNO_3$ equal to ten times the volume of water used to dissolve the salt. This 2nd $Sr(NO_3)_2$ was separated by decantation of the supernatant liquid and washed again with small portions of acetone. After drying and weighing, the dissolution, concentrated nitric acid addition and acetone washings steps were repeated to give a 3rd $Sr(NO_3)_2$ precipitate.

Further purification of the Sr from barium, radium and lead contaminants was performed by a Ba chromate precipitation from an acetate-buffered solution at pH 5. A final clean-up of the Sr from ingrown Y-90 and some other possible beta-emitting radionuclides (e.g., Bi-210) was made by an iron hydroxide scavenge using 10 - 50 mg of Fe(III) and concentrated ammonia to pH 9. The iron hydroxide precipitate was centrifuged off and the Sr-acetate-chromate solution was acidified with concentrated HCl to pH 1. The purified Sr fraction was diluted with 0.1 M HCl. The chemical recovery of the Sr was determined by X-Ray fluorescence on a sample aliquot.

*Milking of $^{90}Y$ from the purified strontium fraction*

This step consists in the separation of the produced $^{90}Y$ from the $^{90}Sr$ contained in the solution. For that reason, an ingrowth period of 2 - 3 weeks was allowed before separation of the $^{90}Y$. Then, the Sr solution was transferred to a beaker. An accurately known amount of yttrium carrier (10 mg) was added and the solution was evaporated down to 20 ml. The solution was transferred to a centrifuge tube, 1 g of $NH_4Cl$ was dissolved in it and concentrated $NH_4OH$ was added to pH 9 to precipitate yttrium hydroxide. The supernatant solution was decanted away from the Y hydroxide precipitate. The time at which the decantation occurred was noted as the Y-Sr separation time.

After the Y hydroxide dissolution with concentrated HCl, the solution was diluted to 25 mL, and 1 g of $NH_4Cl$ was dissolved in it. Ten mg of stable Sr holdback carrier were added and a second mixed Y hydroxide was precipitated with $NH_4OH$. The flocculated precipitate was centrifuged and the supernatant solution was decanted. This 2nd Y hydroxide was dissolved in concentrated HCl, diluted and filtered through a membrane filter to remove any insoluble material.

To the Y solution, 0.5 g of oxalic acid was added, the solution was heated and a white yttrium oxalate was precipitated by the addition of $NH_4OH$ to pH 1.5 - 2. This preliminary yttrium oxalate is separated from the solution by filtration through a membrane filter. Then it was dissolved by treatment with concentrated HCl and passed through the filter with rinses into a 100 ml beaker. The final yttrium oxalate precipitate was obtained from 40 - 50 mL of hot solution by dissolving 0.1 g of oxalic acid and adding concentrated ammonia until pH 1.5 - 2. The yttrium oxalate was digested for about 30 minutes to obtain a crystalline form. Then it was filtered onto a pre-washed, pre-weighed 0.2 $\mu$m polysulfone membrane filter (22 mm diameter, Gellman Sciences, Inc.). The yttrium oxalate was washed with 0.5 % ammonium oxalate solution and 80 % ethanol.

The final filtered yttrium oxalate was dried in a 70 °C oven for ca. 30 minutes and weighed to determine the yttrium chemical recovery from the stable weighing form of $Y_2(C_2O_4)_3 \cdot 9\ H_2O$ (10 mg of Y gives 34 mg of yttrium oxalate). Then, the yttrium oxalate-loaded filter was mounted to fit in a Risoe GM-25-5 Beta Multicounter System (Riso National Laboratory, Roskilde, Denmark), a gas-flow proportional counter with anti-coincidence background reduction. Counting generally starts 6 to 8 hours after the Y-Sr separation time. The measured beta-activity decay curve must be consistent with the known 64 hour half-life of $^{90}Y$ which indicates the high radiochemical purity of the yttrium sources.

**(7) Tritium analysis**

One liter seawater samples were collected in plastic bottles, tightly sealed and transferred to MEL for storage before analysis. Samples were then sent to Dr. Jurgen Sültenfuß, , University of Bremen, for analysis in the Bremen Mass Spectrometric Facility for tritium analysis using the He-3 ingrowth method (Figure 3.11.14, Sültenfuß et al., 2005). For ingrowth of tritiugenic $^3He$ in the laboratory, typically 500 mL are sucked into an evacuated 1-L soda-glass bulb. The contained helium is removed (to $< 10^{-6}$ of solubility equilibrium concentration) by flushing the head space with water vapour under heavy shaking for 30 min, where after the bulb is flame sealed. The shaking ensures timely escape of dissolved helium into the head space. The flushing (50 mL/s) is enforced by pumping through a capillary connection that regulates the flow, and, together with a

narrowing in the bulb's head tubing, prevents any diffusion back into the bulb; the resulting water loss amounts to about 2 g, so that isotopic tritium fractionation remains negligible. Beforehand, the bulb's walls are made helium-free by heating the bulb in vacuo to 400 °C for 24 hours. After typically a six-month storage, enough tritiugenic $^{3}He$ has been generated to obtain a tritium detection limit of 10 mTU. Any $^{3}He$ other than tritiugenic is corrected for using a concurrent measurement of $^{4}He$ (the $^{3}He$ / $^{4}He$ ratio is approximately the atmospheric one). That correction is a prerequisite for precise measurement of the minute amounts of tritiugenic $^{3}He$ produced.

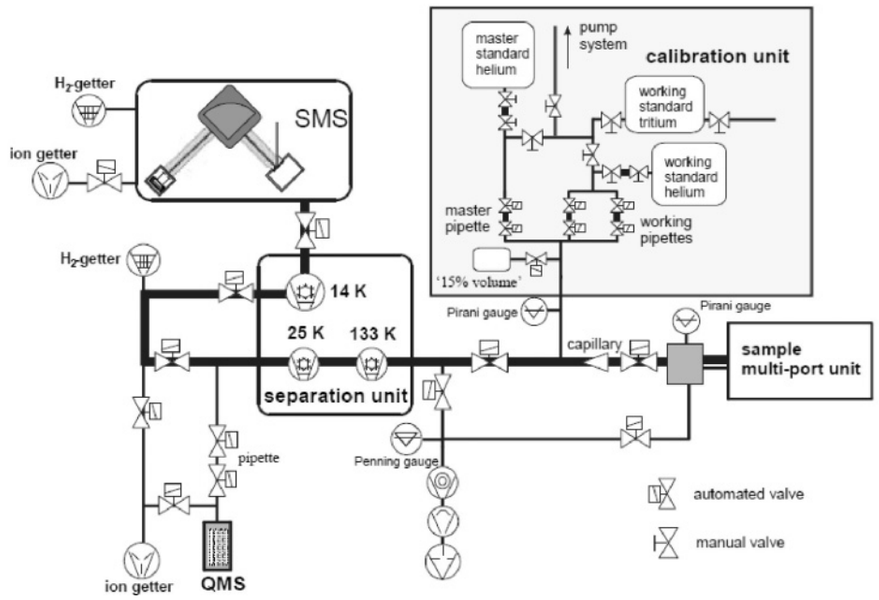


Figure 3.11.14. Scheme of the mass spectrometry system used for tritium analysis (Sültenfuß et al., 2005).

### 3.11.4 Analyses at Korean Institute of Nuclear Safety (KINS) in South Korea

C. S. Kim (KINS)

**(1) Personnel**

C. S. Kim: Korean Institute of Nuclear Safety (KINS)

**(2) Sample preparation**

*Iron hydroxide precipitation*

Weight of the acidified and filtered seawater was determined and poured into the seawater treatment cistern, and then 30 mg of $Fe^{3+}$ carrier added. After stirring for 1 hour, Pu was co-precipitated with $Fe(OH)_3$ by addition of $NH_4OH$ up to pH 8-9. $Fe(OH)_3$ precipitate was collected with 5 L beaker and then heated until boiling on a hot plate. With heating, the pH of suspension was re-adjusted to pH 8 with HCl. After cooling, supernatant was discarded by decantation and the $Fe(OH)_3$ was recovered on a glass fiber filter by suction filtration, and then the precipitate was dissolved with conc. HCl. The dissolved solution was dried on a hot plate and then dissolved with 12 mL 5 M $HNO_3$. The solution was filtered with a membrane filter (0.45 $\mu$m) and then the oxidation state of Pu was adjusted according to next procedure prior to loading to an on-line automated separation system.

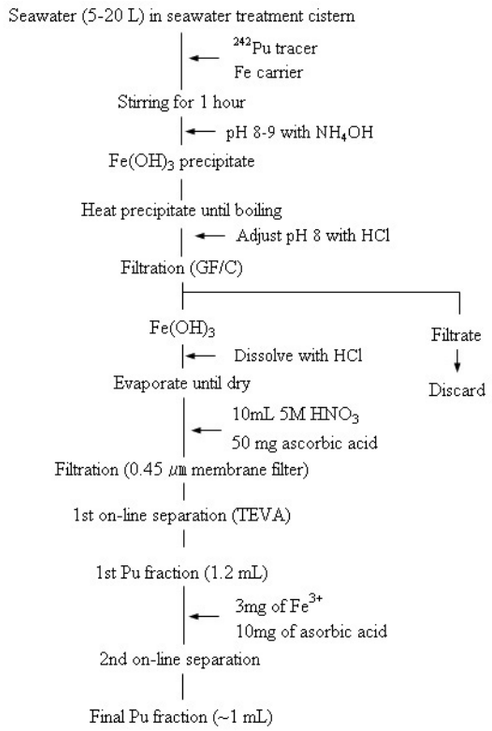


Figure 3.11.15. Pre-treatment of seawater for Pu chemical purification.

*Adjustment of oxidation state of plutonium*

The oxidation state of Pu in the loading solution was kept to +4 oxidation state by dissolving with 5 M $HNO_3$ and extra high oxidation state (VI) was reduced to (IV) by the treatment of ascorbic acid. The loading solution was treated with ascorbic acid for at least 20 minutes before loading to on-line separation system.

**(3) Chemical purification**

*Plutonium purification by on-line separation*

Chemical separation was carried out by on-line automated purification system as shown schematically in Figure 3.11.15, which is developed by Kim *et* al. (2002). The on-line automated purification process consist of 10 purification steps including the sample loading, rinsing and elution, which is described in Table 3.11.6. The 5 M $HNO_3$, 1 M $HNO_3$ and 9 M HCl solutions were used to remove U, Th and bulk matrix elements in sample solution, which were injected into TEVA-Spec resin by two peristaltic tubing pumps. Separation column (3 mm i.d. × 25 mm long) of borosilicate column (Omnifit, Cambridge, England) packed with TEVA resin (Eichrom Industries, Inc., Darien, IL, USA) was installed in the on-line purification system.

To minimize the interference effect of $^{238}$U on 239 m/z, the 1st purified Pu fraction was treated once more by the 2nd on-line purification procedure. The 2nd separation is the same as that of the 1st separation process. To adjust matrix and oxidation state of Pu, 3 mg of $Fe^{3+}$ carrier, 1.2 mL 10 M $HNO_3$, 10 mg of ascorbic acid and 2.6 mL 5 M $HNO_3$ were sequentially added to the 1st Pu fraction. Approximately 5 mL 5 M $HNO_3$ was injected into the 2nd on-line purification system.

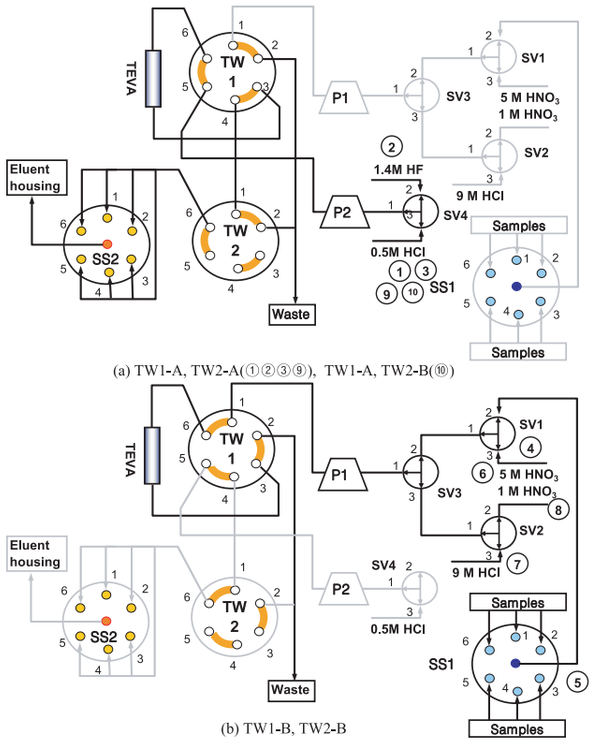


Figure 3.11.16. Schematic diagram of the on-line separation system for Pu isotopes. P1 and P2, peristaltic pump; SS1 and SS2, six-fort solvent selector; TW, two-way valve; SV1 ~ SV4, isolation valve. The circled numbers indicate the procedure order, as described in Table 3.11.6.

Table 3.11.6. Description of sequential separation steps in on-line automated purification for Pu.

| Step | Pumped medium | two-way 6 port valve 1 | two-way 6 port valve 2 | Flow rate/ ml min$^{-1}$ | | SV1 | SV2 | SV3 | SV4 | Time/s |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Pump1 | Pump2 | | | | | |
| 1 | 0.5 M HCl | 2 | 1 | 0 | 0.83 | - | - | - | Bottom | 40 |
| 2 | 1.4 M HF | 2 | 1 | 0 | 0.83 | - | - | - | Top | 90 |
| 3 | 5 M $HNO_3$ | 1 | 2 | 1.6 | 0 | - | - | - | Bottom | 50 |
| 4 | 5 M $HNO_3$ | 1 | 2 | 1.6 | 0 | Bottom | - | Top | - | 240 |
| 5 | 5 M $HNO_3$ | 1 | 1 | 1.6 | 0 | Top | - | Top | - | 700 |
| 6 | 5 M $HNO_3$ | 1 | 2 | 1.6 | 0 | Bottom | - | Top | - | 240 |
| 7 | 9 M HCl | 2 | 1 | 0 | 0.83 | - | Bottom | Bottom | - | 100 |
| 8 | 1 M $HNO_3$ | 1 | 1 | 1.6 | 0 | - | Top | Bottom | - | 160 |
| 9 | 0.5 M HCl | 2 | 1 | 0 | 0.83 | - | - | - | Bottom | 6 |
| 10 | 0.5 M HCl | 2 | 2 | 0 | 0.83 | - | - | - | Bottom | 75 |

| | Description of step |
|---|---|
| 1 | 0.5 M HCl is pumped through resin to rinse residual elements. |
| 2 | 1.4 M HF is pumped through resin to rinse residual elements. |
| 3 | 0.5 M HCl is pumped through resin to fill the eluent line and exchange HF solution |
| 4 | 5 M $HNO_3$ is pumped through column to pre-treat resin at 1.6 ml min$^{-1}$. |
| 5 | Sample is loaded to TEVA-Spec at 1.6 ml min$^{-1}$. |
| 6 | 5 M $HNO_3$ is pumped to rinse residual sample and interference materials. |
| 7 | 9 M HCl is pumped through resin to clean Th in resin. |
| 8 | 1 M $HNO_3$ is pumped to rinse residual U. |
| 9 | 0.5 M HCl is pumped through TEVA-Spec to elute Np at 0.83 ml min$^{-1}$ for 6 seconds until 0.5 M HCl reach the two-way valve. |
| 10 | About 1.1 ml 0.5 M HCl is pumped to elute Np and Pu on TEVA-Spec. |

**(4) ICP-MS analysis**

Sample was measured by ICP-SF-MS, a PlasmaTrace 2 (Micromass, Manchester, UK), under the optimum sensitivity and stability. Approximately 1 mL of final Pu fraction was injected into plasma by an Aridus desolvating introduction system (Cetac Technologies, Omaha, NE, USA) involving a T1-H microconcentric nebulizer. The Pu isotopes ($^{239}$Pu, $^{240}$Pu, $^{242}$Pu) and $^{238}$U were measured three times in peak hopping mode. The details of operation condition used for ICP-SFMS and the sample introduction system are described in Table 3.11.7. To increase integrated count, eluent completely used up and sample was measured three runs to get relative standard deviation. Sample blank was positioned in the first row before samples and $^{242}$Pu standard solutions were finally measured to check the chemical recovery. An example of the mass spectrum for Pu isotopes and $^{238}$U obtained by ICP-SF-MS is shown in Figure 3.11.17. The concentration of Pu isotopes was calculated base on the isotope dilution analysis (IDA) using following equation.

$$C \pm \sigma_c = \left[ (R_s - R_t) \pm \sqrt{(\sigma_{Rs})^2 + (\sigma_{Rt})^2} \right] \frac{T}{W}$$

C : Concentration of $^{239}$Pu or $^{240}$Pu (pg/g)

$R_s$ : $([^{239}Pu]_s - [^{239}Pu]_b)/([^{242}Pu]_s - [^{242}Pu]_b)$ or

$([^{240}Pu]_s - [^{240}Pu]_b)/([^{242}Pu]_s - [^{242}Pu]_b)$

$R_t$ : $([^{239}Pu]_t - [^{239}Pu]_b)/([^{242}Pu]_t - [^{239}Pu]_b)$ or

$([^{240}Pu]_t - [^{240}Pu]_b)/([^{242}Pu]_t - [^{242}Pu]_b)$

s ; sample, b ; blank sample, t ; tracer ( $^{242}$Pu )

$[^{239}Pu]$, $[^{240}Pu]$, $[^{242}Pu]$ : $^{239}$Pu , $^{240}$Pu, $^{242}$Pu count rate (cps)

T : Amounts of tracer added ( $^{242}$Pu ) ( pg )

W : Sample amounts (g)

$\sigma_c$ : $^{239}$Pu or $^{240}$Pu standard deviation ( pg/g )

$\sigma_{Rs}$ : $[^{239}Pu]_s/[^{242}Pu]_s$ or $[^{240}Pu]_s/[^{242}Pu]_s$ standard deviation of sample

$\sigma_{Rt}$ : $[^{239}Pu]_t/[^{242}Pu]_t$ or $[^{240}Pu]_t/[^{242}Pu]_t$ standard deviation of tracer

Table 3.11.7. Operation condition of ICP-SF-MS (PT2).

| | ICP and interface | | | |
|---|---|---|---|---|
| RF power, W | 1350 | | | |
| Coolant gas flow, L/min | 14 | | | |
| Auxiliary gas flow, L/min | 2.2 | | | |
| Carrier gas flow, L/min | 1.1 | | | |
| Expansion chamber pressure, mbar | 1.6 | | | |
| | Aridus | | | |
| Sweeping gas flow. L/min | 2.4 | | | |
| Spray chamber temp., °C | 80 | | | |
| Membrane desolvator temp., °C | 160 | | | |
| Sample uptake rate, mL/min | 0.1 | | | |
| Type of nebulizer | T1 | | | |
| | date acquisition | | | |
| Element | $^{238}$U | $^{239}$Pu | $^{240}$Pu | $^{242}$Pu |
| Mass range, amu | 237.8 - 238.6 | 238.4 - 239.6 | 239.4 -240.6 | 241.4 - 242.6 |
| Dwell time, ms | 7 | 60 | 120 | 15 |
| Width Points | 100 | 100 | 100 | 100 |
| Peak widths | 1.7 | 1.6 | 1.6 | 1.8 |
| Sweep no. | 3 | | | |
| Runs | 3 | | | |
| Resolving Power | 430 | | | |
| Total analysis time, s/sample | 3.57 | 28.8 | 57.6 | 8.1 |

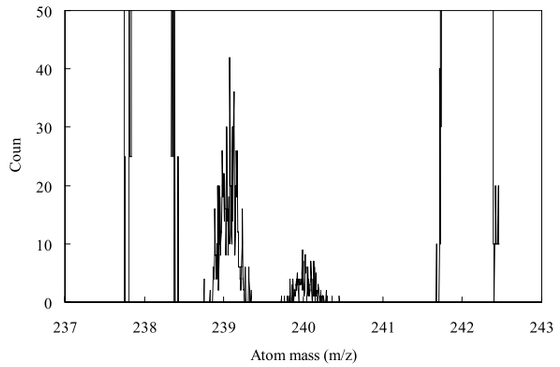


Figure 3.11.17. Mass spectrum of plutonium isotopes and $^{238}U$ in deep (600 meter) seawater.

## 3.11.5 Preliminary results of $^{137}Cs$ and Pu isotopes in the surface layers

M. Aoyama (MRI), M. Eriksson (IAEA-MEL), J. Gastaud (IAEA-MEL), K. Hirose (MRI, LLRL), Y. Hamajima (LLRL), C. S. Kim (KINS), K. Komura (LLRL), I. Levy-Palomo (IAEA-MEL), P. P. Povinec (Comenius Univ. of Bratislava), S. Rezzoug (IAEA-MEL), P. Ross (RNL), J. A. Sanchez-Cabeza (IAEA-MEL), and I. Sykora (Comenius Univ. of Bratislava)

### (1) Personnel

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K. Hirose: MRI, LLRL

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K. Komura: LLRL

I. Levy-Palomo: IAEA-MEL

P. P. Povinec: Comenius University of Bratislava

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P. Ross: RNL

J. A. Sanchez-Cabeza: IAEA-MEL

I. Sukora: Comenius University of Bratislava

### (2) Preliminary results of $^{137}Cs$ along the BEAGLE lines

$^{137}Cs$ concentrations in surface waters in the mid latitude region of the Southern Ocean along P06, A10 and I03/4 lines are shown in Figure 3.11.18. Those were in the range from 0.1 to 2.3 Bq $m^{-3}$, which is no significant difference with that in the North Pacific mid-latitude region (Aoyama et al., 2004, 2006; Povinec et al., 2003). Large $^{137}Cs$ concentration gradients, with high values in the North Pacific mid-latitude region, and low ones in the South Pacific were observed in the 1970s and 1980s (Bowen et al., 1980; Hirose and Aoyama, 2003).

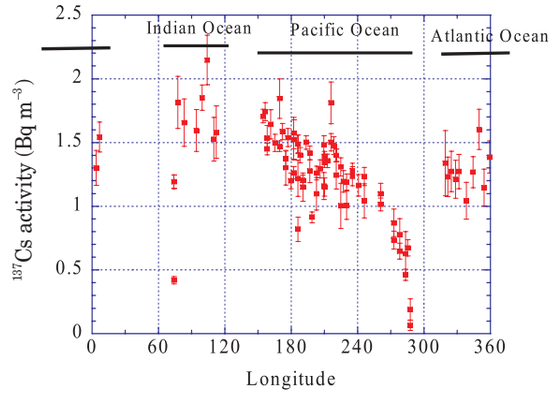


Figure 3.11.18. $^{137}Cs$ concentration in the surface layers, surface and 100 m depth, along BEAGLE lines in 2003/2004.

The high density $^{137}$Cs data revealed a typical longitudinal distribution as shown in Fig. 3.11.18, which depends on sea areas. In the Pacific Ocean, the $^{137}$Cs concentrations in the Tasman Sea, 155 deg. E to 180 deg. E, ranged from 1.37 to 1.74 Bq m$^{-3}$, showing higher values compared with that in the subtropical gyre in the South Pacific. In the Tasman Sea, the $^{137}$Cs concentrations gradually decreased from west to east, which corresponds from upstream and downstream of East Australian Current System (EAC), respectively. The surface $^{137}$Cs concentration was high in the upstream of EAC and low in the downstream of EAC. In the subtropical gyre, there was no longitudinal gradient of the surface $^{137}$Cs concentrations, which ranged from 0.91 to 1.53 Bq m$^{-3}$, although the surface $^{137}$Cs levels varied spatially. In the Eastern South Pacific, the $^{137}$Cs concentrations, ranged from 0.07 to 1.14 Bq m$^{-3}$, showing lower values than that in the Tasman Sea and subtropical gyre.

In the Indian Ocean, the $^{137}$Cs concentrations ranged from 1.5 to 2.2 Bq m$^{-3}$, showing higher values compared with that in the Southern Hemisphere. The $^{137}$Cs concentrations in the Mozambique Channel ranged from 0.4 to 1.2 Bq m$^{-3}$, showing lower values than those in the Indian Ocean and Tasman Sea.

In the Atlantic Ocean, the $^{137}$Cs concentrations ranged from 1.1 to 1.6 Bq m$^{-3}$, showing similar with that in the subtropical gyre in the Pacific Ocean.

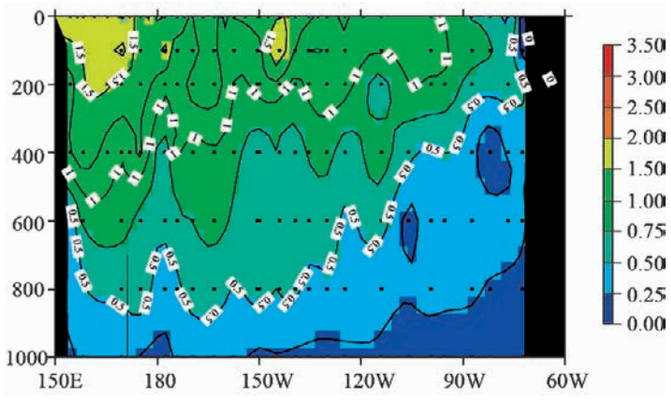


Figure 3.11.19. $^{137}$Cs section in the surface layers, surface - 1000 m depth, along P6 line.

The $^{137}$Cs concentrations in the layers between the surface to 1000 m depth are shown in Figure 3.11.19.

As well as the general trend of $^{137}$Cs concentration in the surface layers (Figure 3.11.18), the $^{137}$Cs concentrations in the Tasman Sea was higher than 1.5 Bq m$^{-3}$ between surface to 200 m depth, showing higher values than those in the subtropical gyre and the Eastern South Pacific. The $^{137}$Cs concentrations in the layers between surface to 200 m depth ranged from 1.0 to 1.5 Bq m$^{-3}$ in the subtropical gyre and it decreased rapidly in the Eastern South Pacific. This tendency that $^{137}$Cs decreased from west to east in general is observed for the depths between the surface to 1000 m depth throughout the Pacific sector.

**(3) Preliminary results of Pu isotopes along the BEAGLE lines**

$^{239,240}$Pu concentrations in surface water in the mid-latitudes of the South Pacific were in the range of 0.5 to 4.1 mBq m$^{-3}$. The surface $^{239,240}$Pu in the South Pacific was the same order of magnitude as that in the subtropical gyre in the North Pacific (1.5 to 9.2 mBq m$^{-3}$) (Hirose et al., 2001, 2006; Povinec et al., 2003; Yamada et al., 2006). The observation of the current surface $^{239,240}$Pu concentrations suggests that there has not been a marked inter-hemisphere distribution in the Pacific, although rather large spatial variation of surface $^{239,240}$Pu concentration has been observed.

Close sampling spacing revealed that the surface $^{239,240}$Pu concentration shows a different longitudinal distribution from that of $^{137}$Cs (seen in Fig. 3.11.18). The $^{239,240}$Pu concentrations in the Tasman Sea, ranged from 1.0 to 2.9 mBq m$^{-3}$, showed a similar longitudinal distribution as did $^{137}$Cs. In the subtropical gyre, there was no longitudinal gradient of the surface $^{239,240}$Pu concentrations, which ranged from 0.8 to 4.1 mBq m$^{-3}$, although peaks of the higher $^{239,240}$Pu concentrations were observed near 165 °W and 135 °W. In the Eastern South Pacific, the surface $^{239,240}$Pu concentrations which ranged from 0.5 to 3.2 mBq m$^{-3}$, showed a larger variation than that in the Tasman Sea and subtropical gyre. The surface $^{239,240}$Pu concentrations in the mid-latitude region of the South Pacific broadly decreased from west to east.

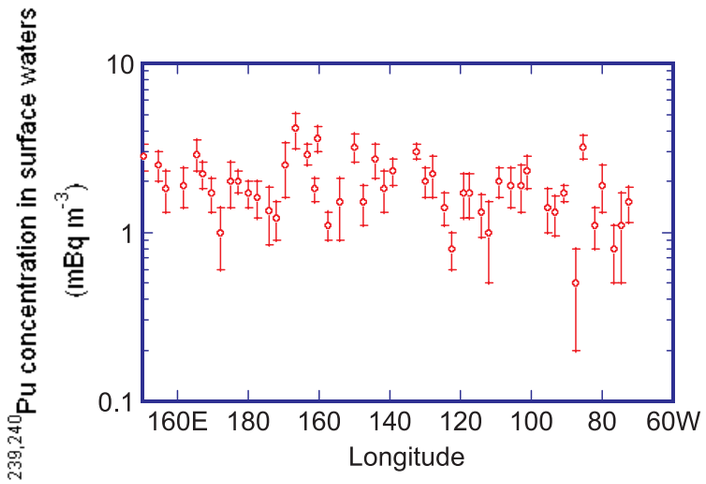


Figure 3.11.20. $^{239,240}$Pu concentration in the surface layers along P6 line.

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# 4. Errata and Updated Data of the Data Books Volume 1 and 2

## 4.1 Errata in the documents

Coefficients of Note 2 in Figure caption of Volume 2 (p. 91) should be corrected as follows.

$a_0 = 6.4409$, $b_0 = -3.9577e{-4}$, $a_1 = 4.3830$, $b_1 = 6.3317e{-4}$

## 4.2 Mistakes in the figures

In Figures 14, 15 and 16 in Volume 2 (vertical sections for dissolved inorganic carbon, total alkalinity and pH), data with quality flags of 6 (mean of replicate measurements) were not included.

## 4.3 Updates in the data files

**(1) FLUOR in the CTD data**

Flags for FLUOR in the CTD exchange format files were wrong (flags for CTDOXV were set by mistake) and corrected.

**(2) pH**

Reporting precision for pH increased from F7.3 to F7.4 (FORTRAN format).

**(3) Total alkalinity and dissolved inorganic carbon**

Following flags and a value for carbon related parameters were revised.

| EXPOCODE | STNNBR | CASTNO | SAMPNO | PARAMETER: Change |
|---|---|---|---|---|
| 49MR03K04_1 | 172 | 1 | 4 | ALKALI_FLAG_W: 2 -> 3 |
| 49MR03K04_1 | 172 | 1 | 1 | ALKALI_FLAG_W: 2 -> 3 |
| 49MR03K04_1 | X15 | 1 | 6 | ALKALI_FLAG_W: 2 -> 3 |
| 49MR03K04_1 | 150 | 1 | 16 | ALKALI_FLAG_W: 2 -> 3 |
| 49MR03K04_1 | 137 | 1 | 1 | ALKALI_FLAG_W: 2 -> 3 |
| 49MR03K04_2 | 95 | 1 | 1 | ALKALI: 2291.3 -> 2381.2 |
| 49MR03K04_2 | 59 | 1 | 33 | ALKALI_FLAG_W: 2 -> 3 |
| 49MR03K04_2 | 59 | 1 | 14 | ALKALI_FLAG_W: 2 -> 3 |
| 49MR03K04_2 | 47 | 1 | 27 | ALKALI_FLAG_W: 2 -> 4 |
| 49MR03K04_2 | 11 | 1 | 9 | TCARBN_FLAG_W: 2 -> 3 |
| 49MR03K04_4 | 7 | 1 | 17 | ALKALI_FLAG_W: 2 -> 3 |
| 49MR03K04_4 | 9 | 1 | 19 | ALKALI_FLAG_W: 2 -> 3 |
| 49MR03K04_4 | 11 | 1 | 19 | ALKALI_FLAG_W: 2 -> 3 |
| 49MR03K04_4 | 11 | 1 | 15 | ALKALI_FLAG_W: 6 -> 3 |
| 49MR03K04_4 | X17 | 1 | 13 | ALKALI_FLAG_W: 2 -> 4 |
| 49MR03K04_4 | 18 | 1 | 16 | TCARBN_FLAG_W: 2 -> 3 |
| 49MR03K04_4 | 27 | 1 | 32 | TCARBN_FLAG_W: 2 -> 3 |
| 49MR03K04_4 | 27 | 1 | 12 | ALKALI_FLAG_W: 2 -> 3 |
| 49MR03K04_4 | 33 | 1 | 1 | ALKALI_FLAG_W: 2 -> 3 |
| 49MR03K04_4 | 38 | 1 | 22 | ALKALI_FLAG_W: 2 -> 3 |
| 49MR03K04_4 | 38 | 1 | 15 | ALKALI_FLAG_W: 6 -> 3 |
| 49MR03K04_4 | 38 | 1 | 3 | ALKALI_FLAG_W: 2 -> 4 |

## 4.4 Planned updates

In the future, data of total organic carbon (TOC) will be available through our web site: http://www.jamstec.go.jp/iorgc/ocorp/data/beagle2003/index.html. In addition, data of the artificial radionuclides will be updated.

# Figure captions

Figure 1 Observation lines for WHP P6, A10 and I3/I4 revisit in Blue Earth Global Expedition 2003 (BEAGLE2003) with bottom topography based on ETOPO5 (Data announcement 88-MGG-02,1988).

Figure 2 Station locations for WHP P6, A10 and I3/I4 revisit in BEAGLE2003 with bottom topography based on Smith and Sandwell (1997).

Figure 3 CFC-11 ($CCl_3F$ ; pmol $kg^{-1}$) cross section. Data with quality flags of 2 and 6 were plotted. Vertical exaggeration of the 0-6,500 m section is 1000:1. Expanded section of the upper 1000 m is made with a vertical exaggeration of 2500:1.

Figure 4 Same as Figure 3 but for CFC-12 ($CCl_2F_2$ ; pmol $kg^{-1}$)

Figure 5 Same as Figure 3 but for $\Delta^{14}$ C of dissolved inorganic carbon (‰).

Figure 6 Same as Figure 3 but for $\delta^{13}$ C of dissolved inorganic carbon (‰).

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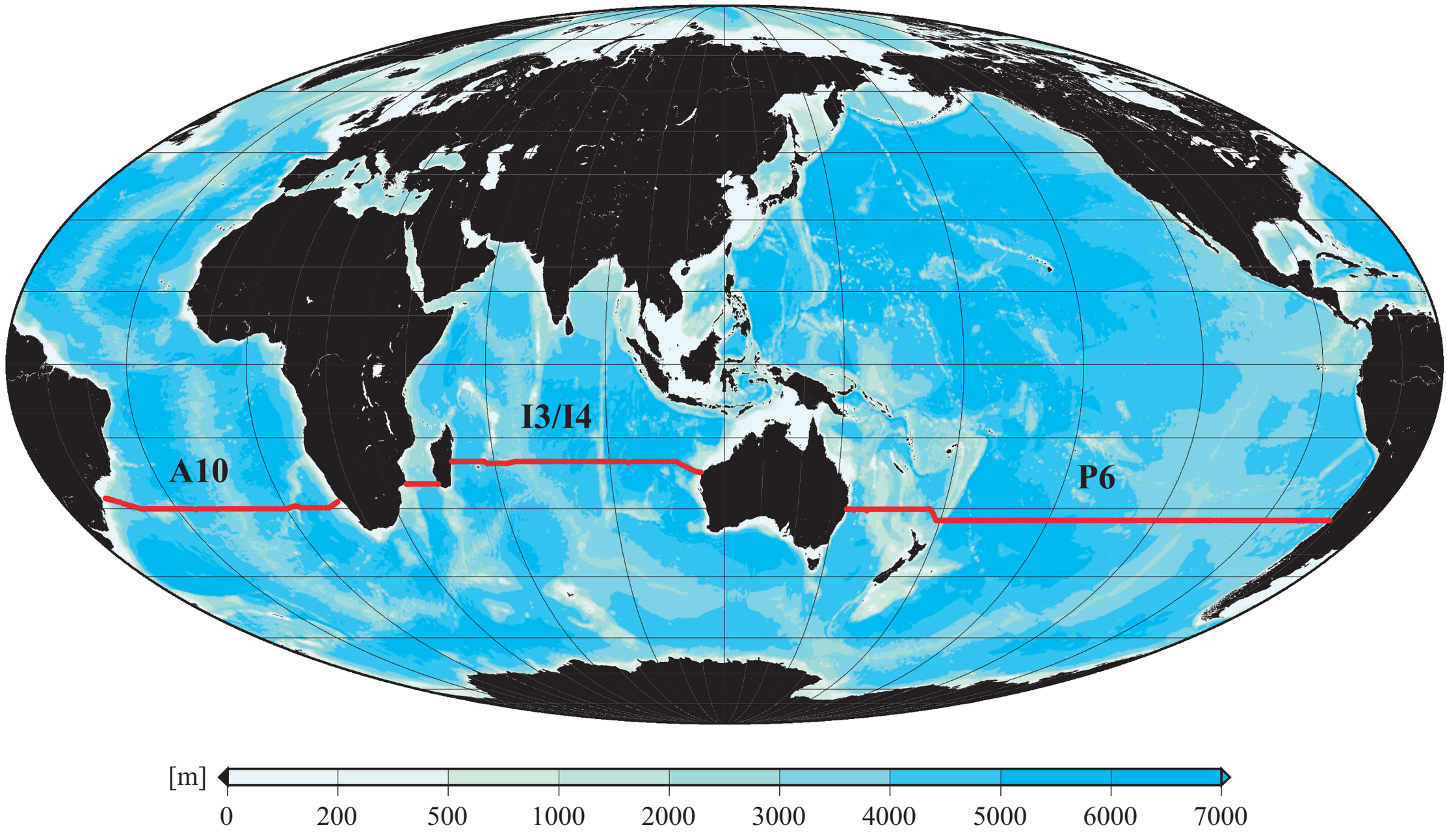
Smith, W. H. F. and D. T. Sandwell (1997): Global seafloor topography from satellite altimetry and ship depth soundings, Sciense, 277, 1956-1962.

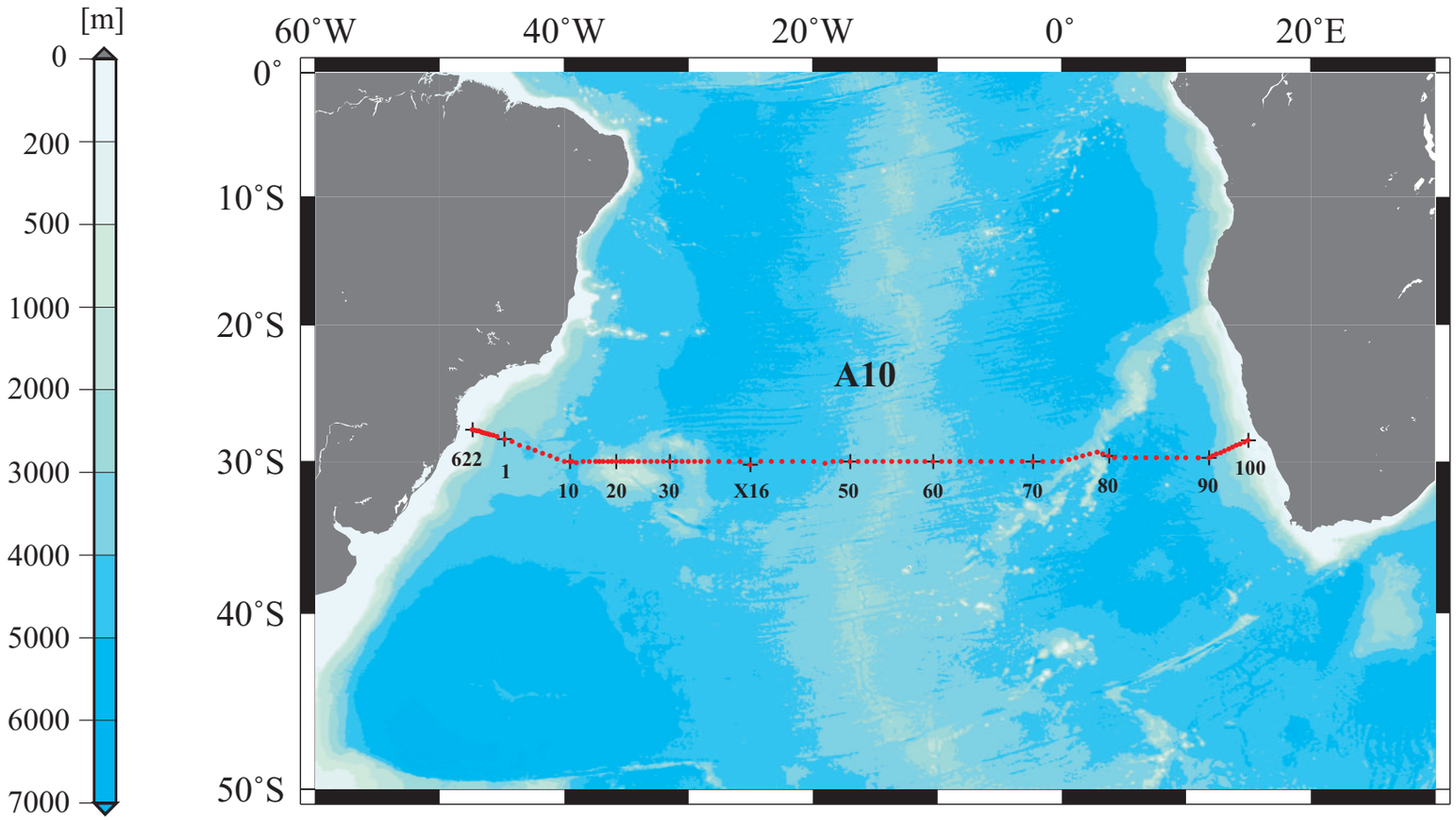
Figure 1

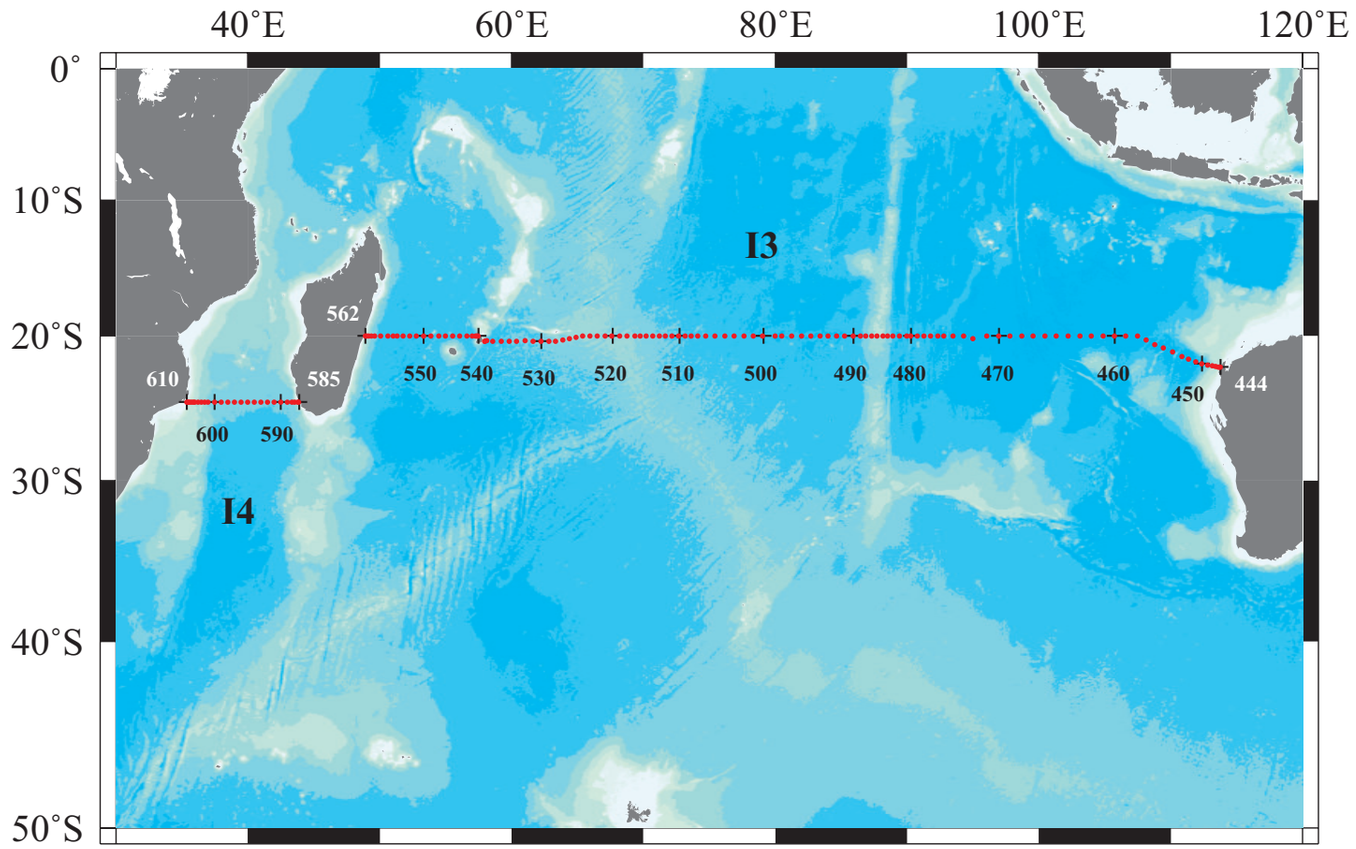



**OBSERVATION LINES FOR WHP P6, A10, I3/I4 REVISIT IN 2003**

Figure 2

# STATION LOCATIONS FOR WHP P6, A10, I3/I4 REVISIT IN 2003




40˚E
60˚E
80˚E
100˚E
120˚E
0˚
10˚S
20˚S
30˚S
40˚S
50˚S
I3
I4
562
610
585
600
590
550
540
530
520
510
500
490
480
470
460
450
444

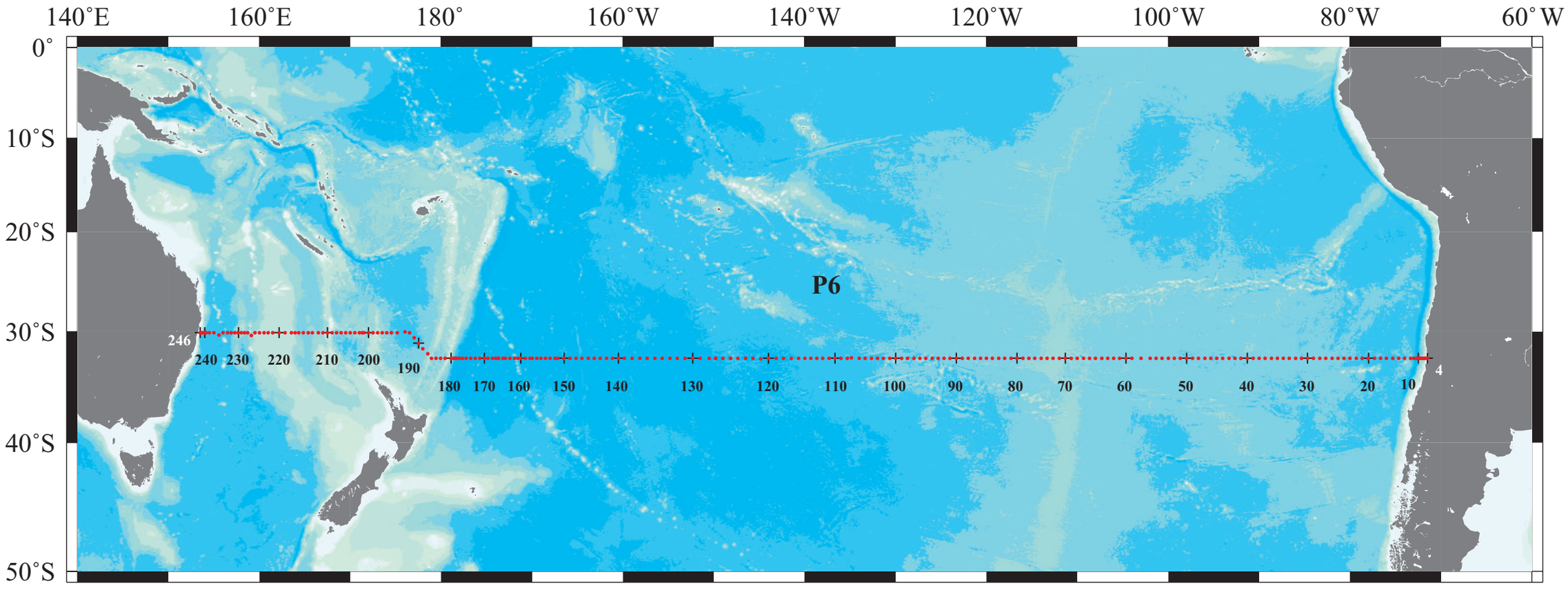
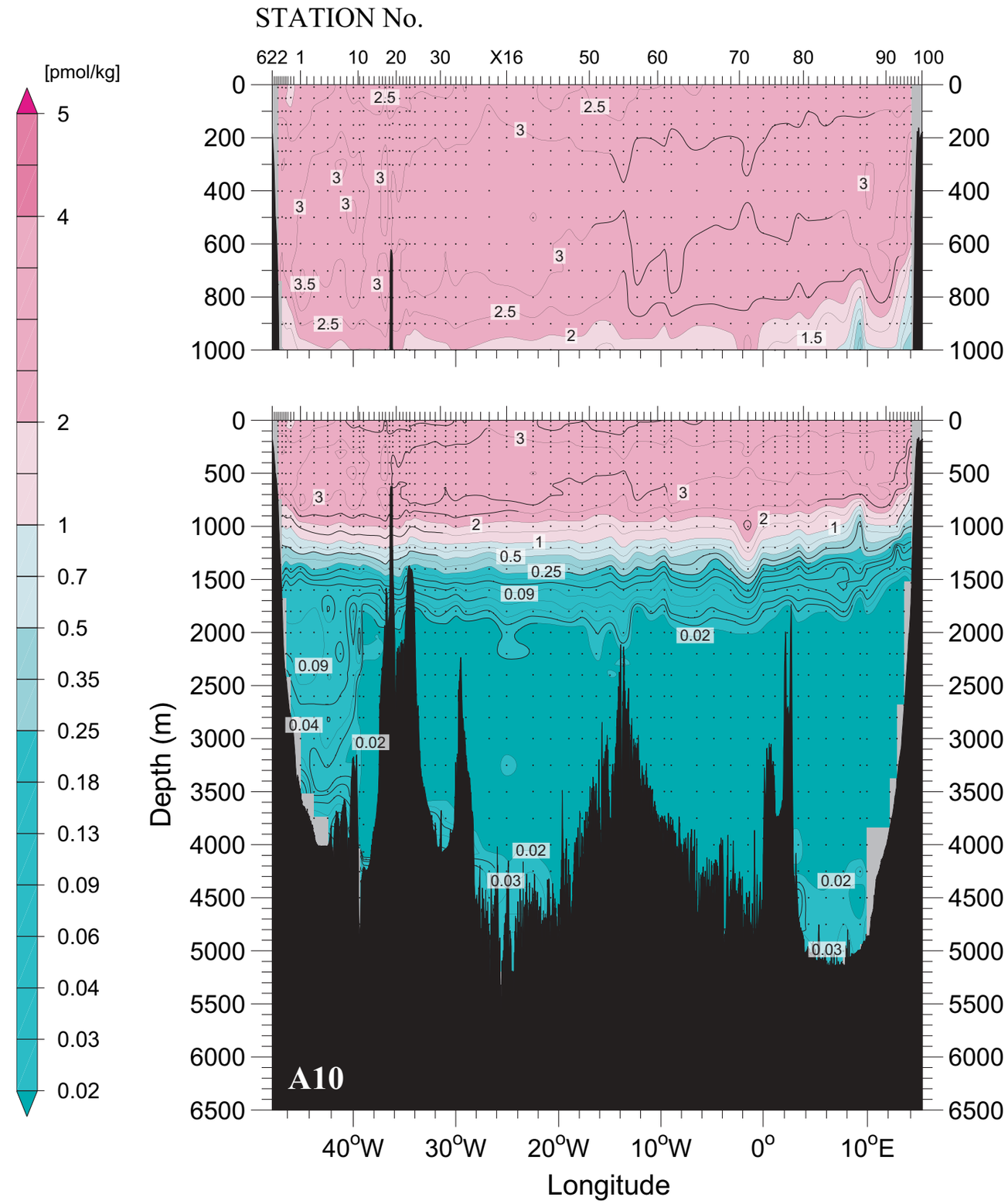
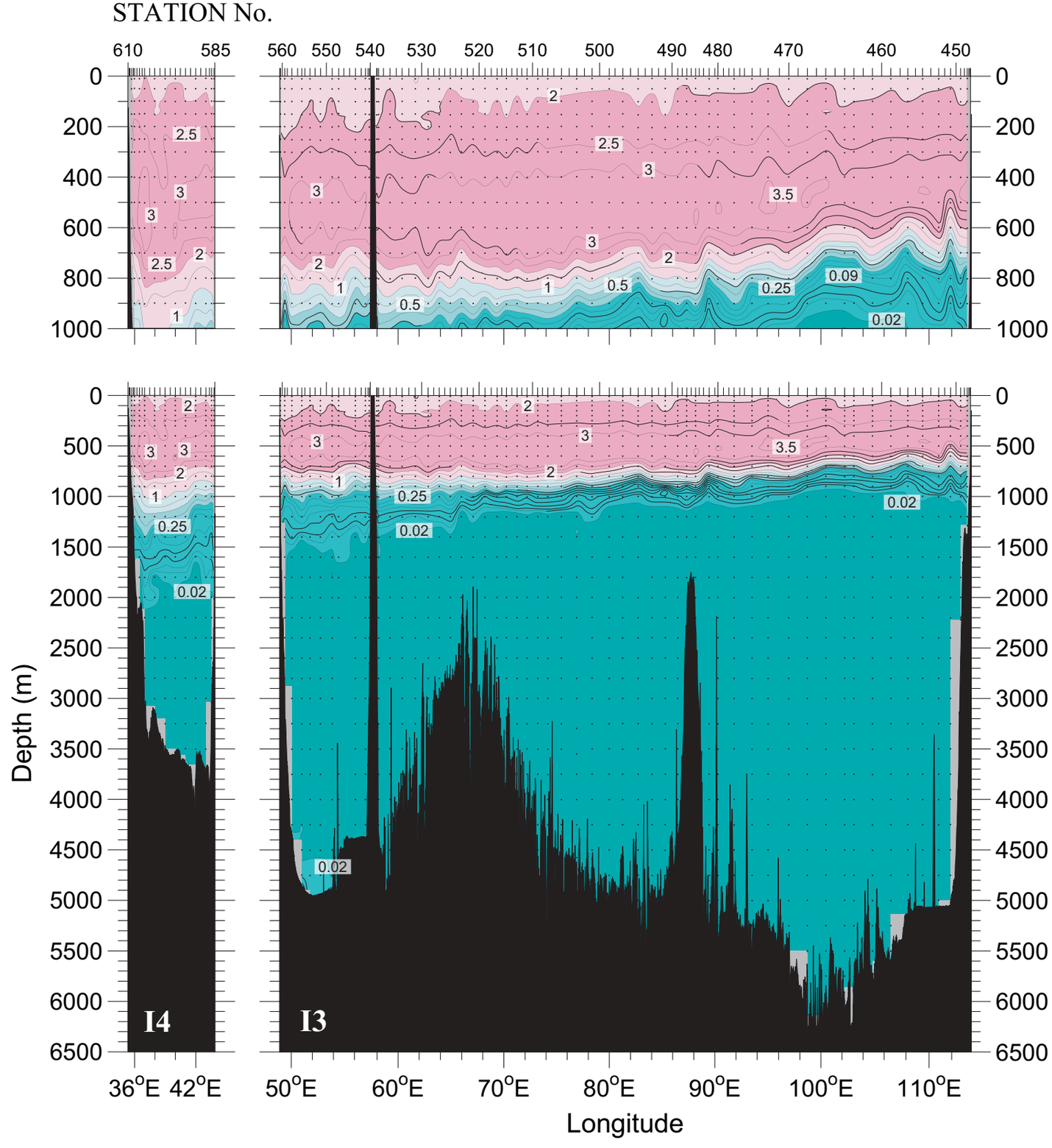

140°E
160°E
180°
160°W
140°W
120°W
100°W
80°W
60°W
0°
10°S
20°S
30°S
40°S
50°S
P6
246
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
4

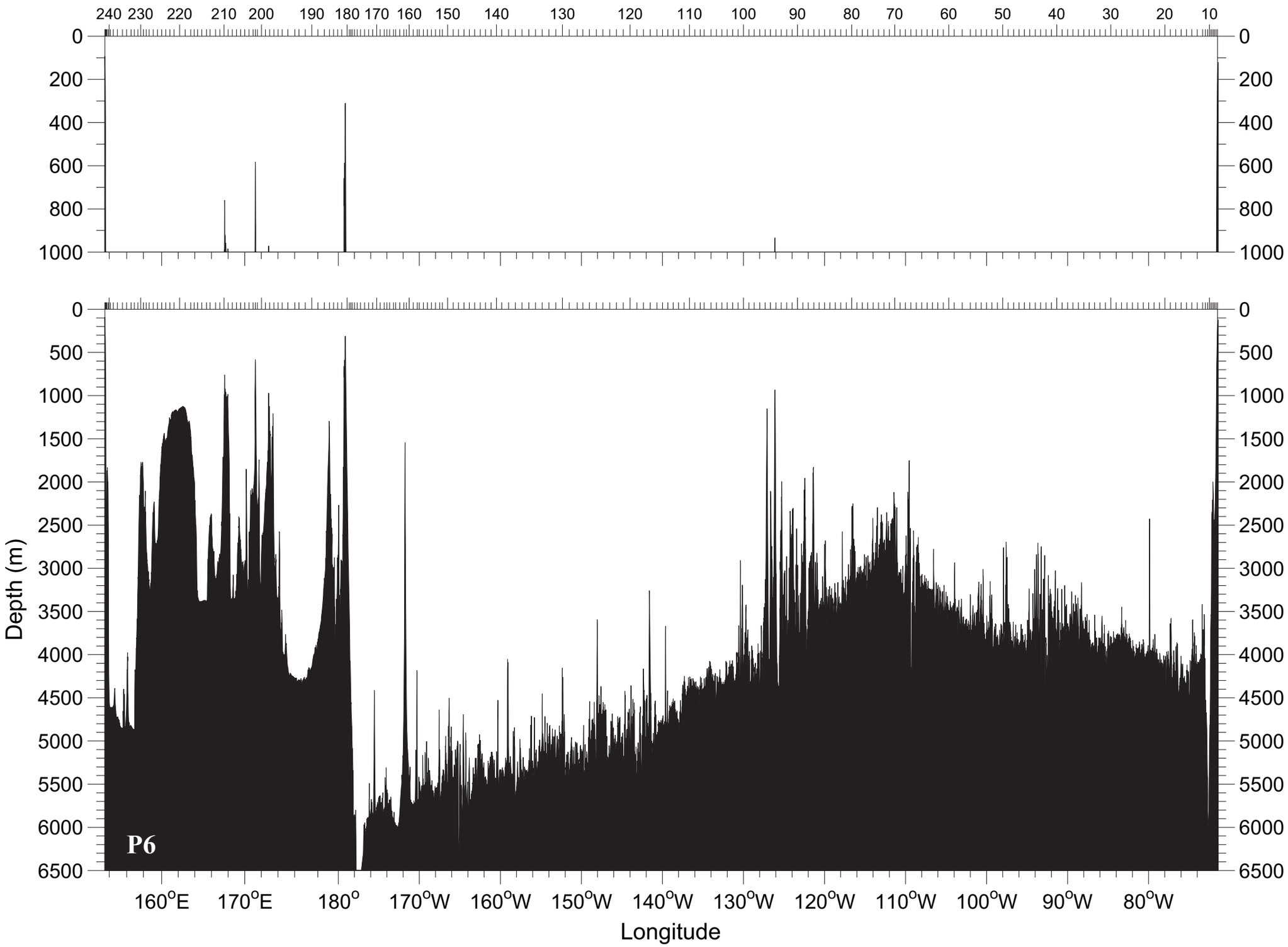
**Figure 3**

**CFC-11 [pmol kg$^{-1}$]**



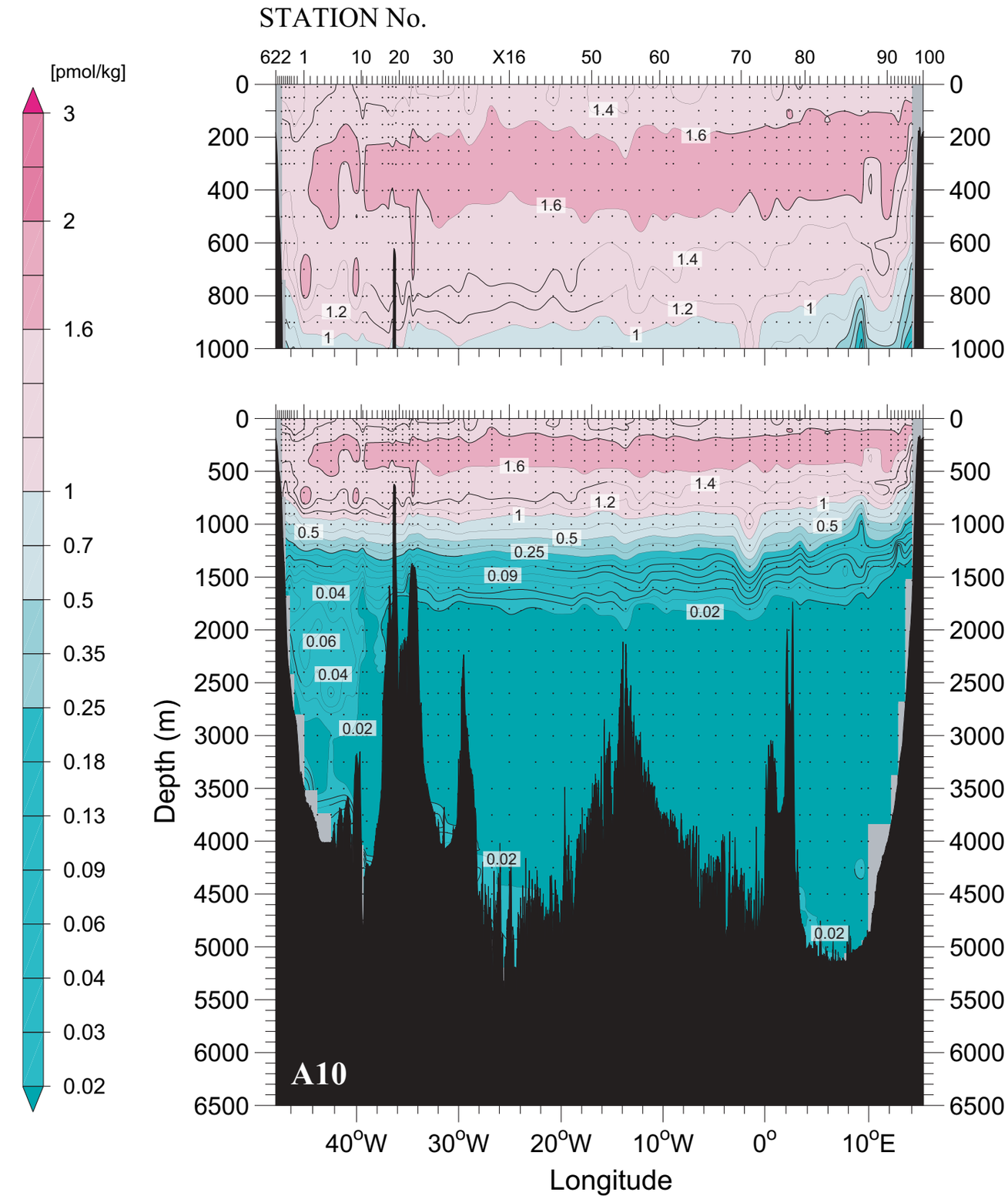

STATION No.
610
585
560
550
540
530
520
510
500
490
480
470
460
450
I4
I3
Depth (m)
Longitude
36°E
42°E
50°E
60°E
70°E
80°E
90°E
100°E
110°E

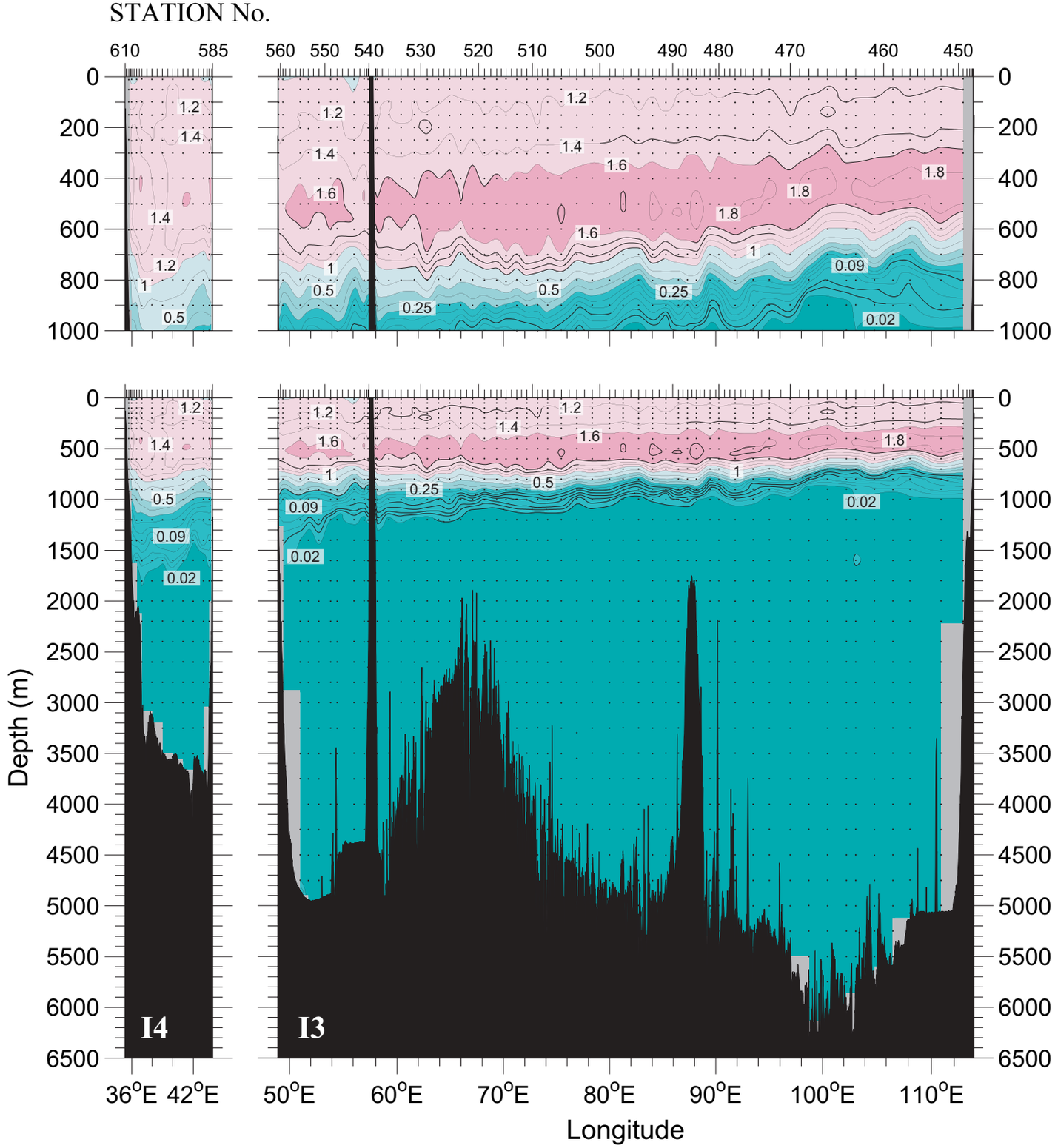
STATION No.


240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
0 200 400 600 800 1000
0 500 1000 1500 2000 2500 3000 3500 4000 4500 5000 5500 6000 6500
Depth (m)
P6
160°E 170°E 180° 170°W 160°W 150°W 140°W 130°W 120°W 110°W 100°W 90°W 80°W
Longitude

# Figure 4

## CFC-12 [pmol kg$^{-1}$]




STATION No.
610
585
560
550
540
530
520
510
500
490
480
470
460
450
Depth (m)
Longitude
36°E
42°E
50°E
60°E
70°E
80°E
90°E
100°E
110°E
I4
I3

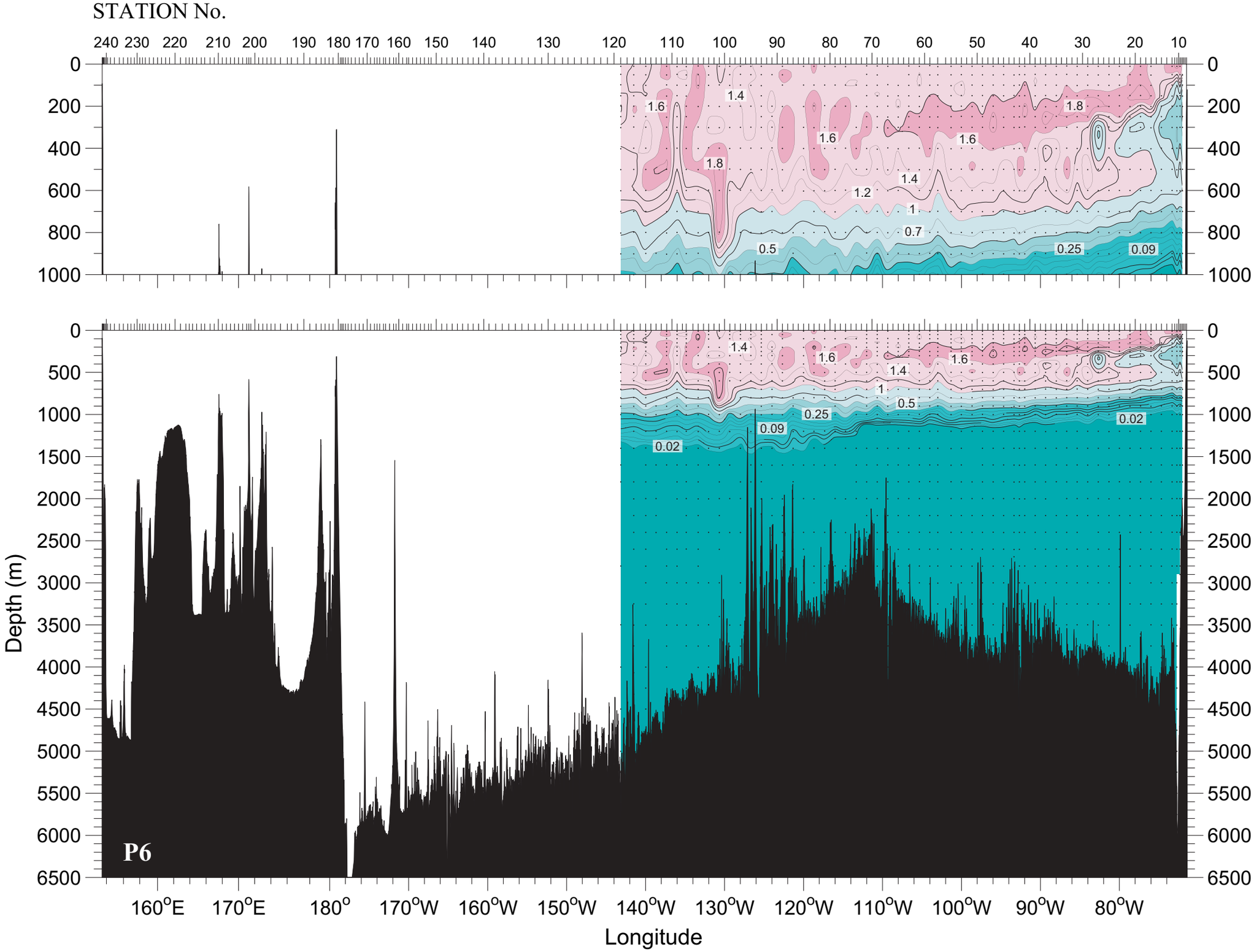
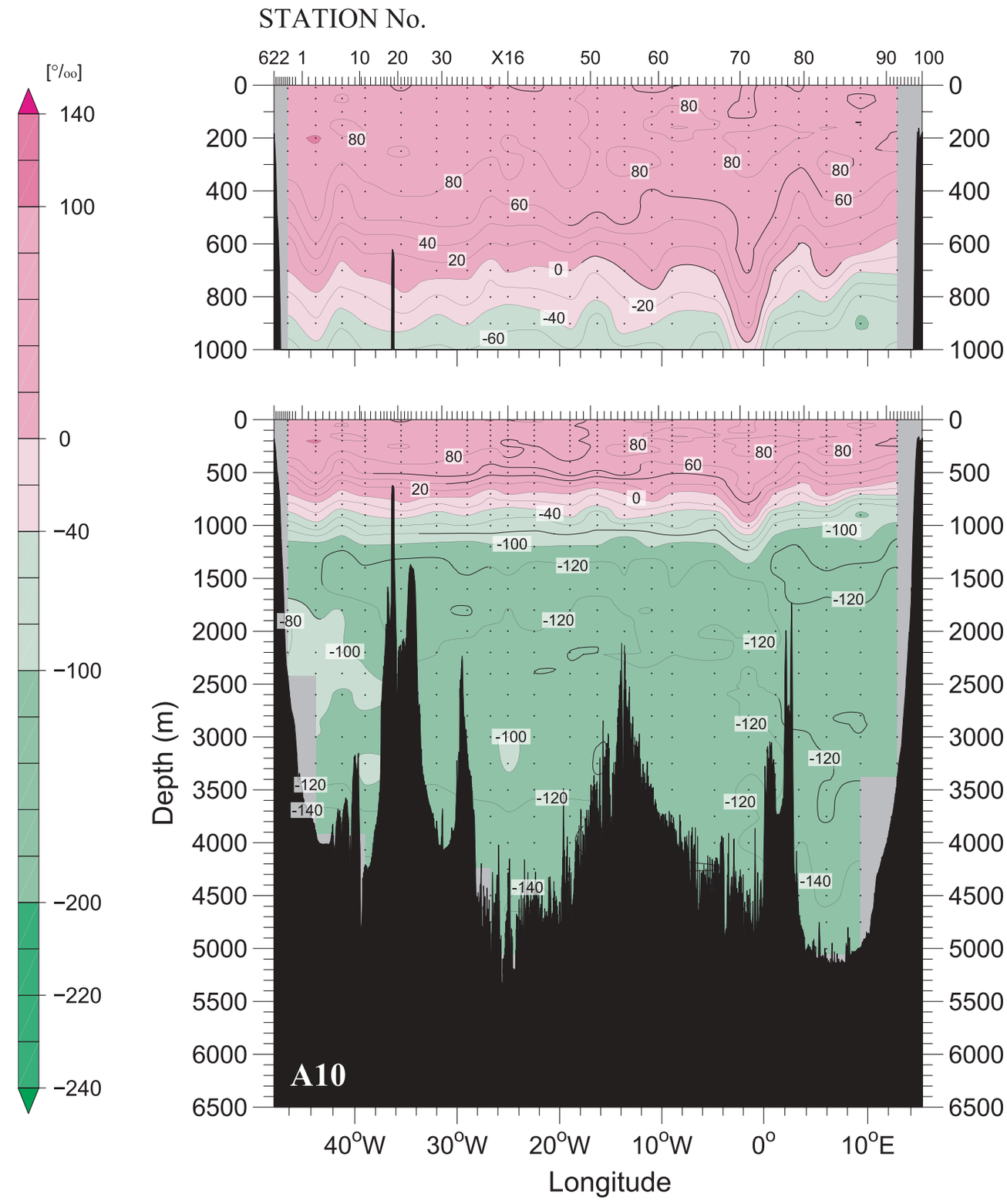
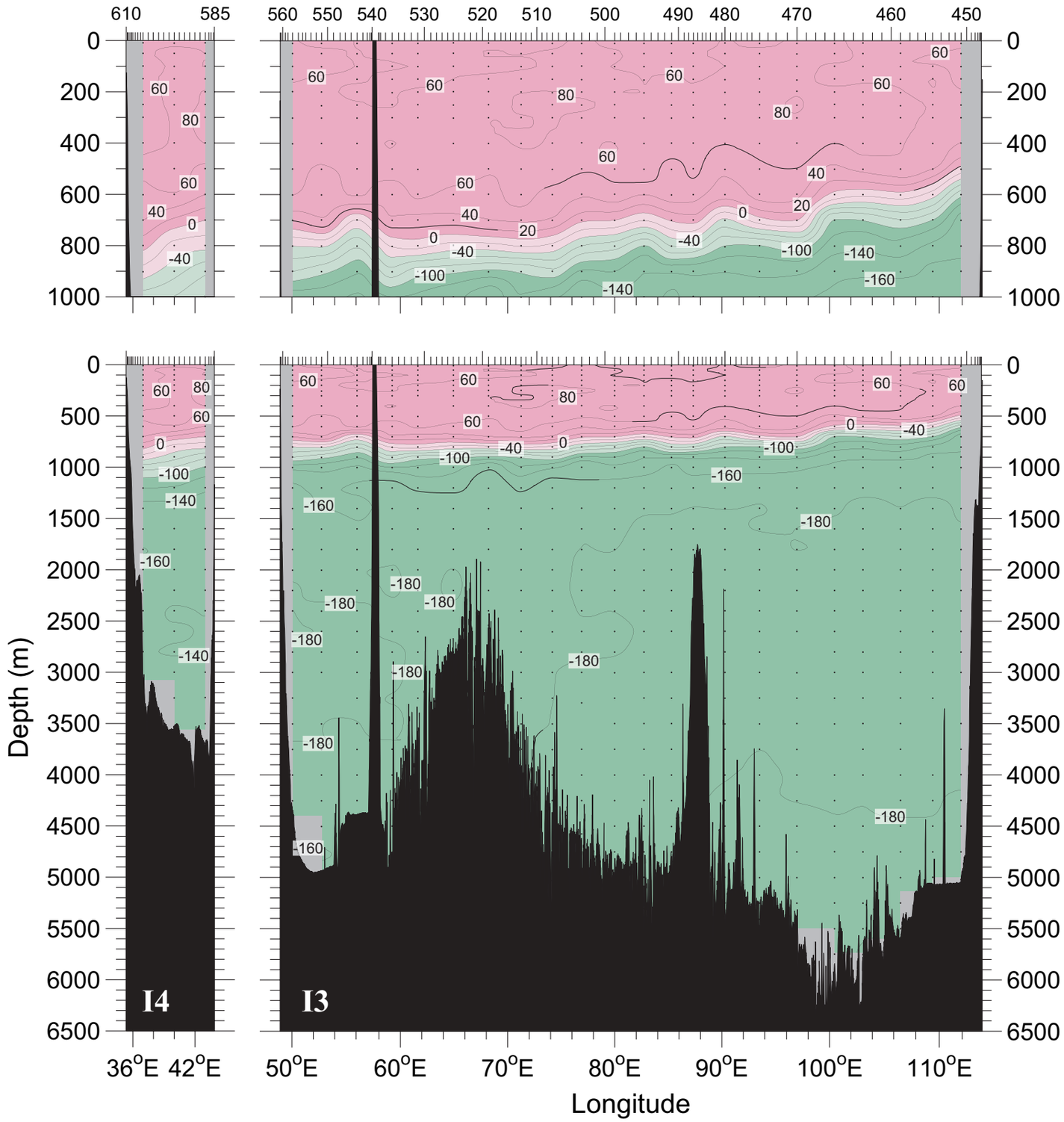

STATION No.
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
0 200 400 600 800 1000
1.6 1.4 1.6 1.8 1.6 1.8 1.4 1.2 1 0.7 0.5 0.25 0.09
0 500 1000 1500 2000 2500 3000 3500 4000 4500 5000 5500 6000 6500
1.4 1.6 1.6 1.4 1 0.5 0.25 0.09 0.02 0.02
Depth (m)
P6
160°E 170°E 180° 170°W 160°W 150°W 140°W 130°W 120°W 110°W 100°W 90°W 80°W
Longitude

**Figure 5**

$\Delta^{14}C$ [‰]



STATION No.


610
585
560
550
540
530
520
510
500
490
480
470
460
450
I4
I3
Depth (m)
Longitude
36°E
42°E
50°E
60°E
70°E
80°E
90°E
100°E
110°E

STATION No.

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

Depth (m)

0 200 400 600 800 1000 1500 2000 2500 3000 3500 4000 4500 5000 5500 6000 6500

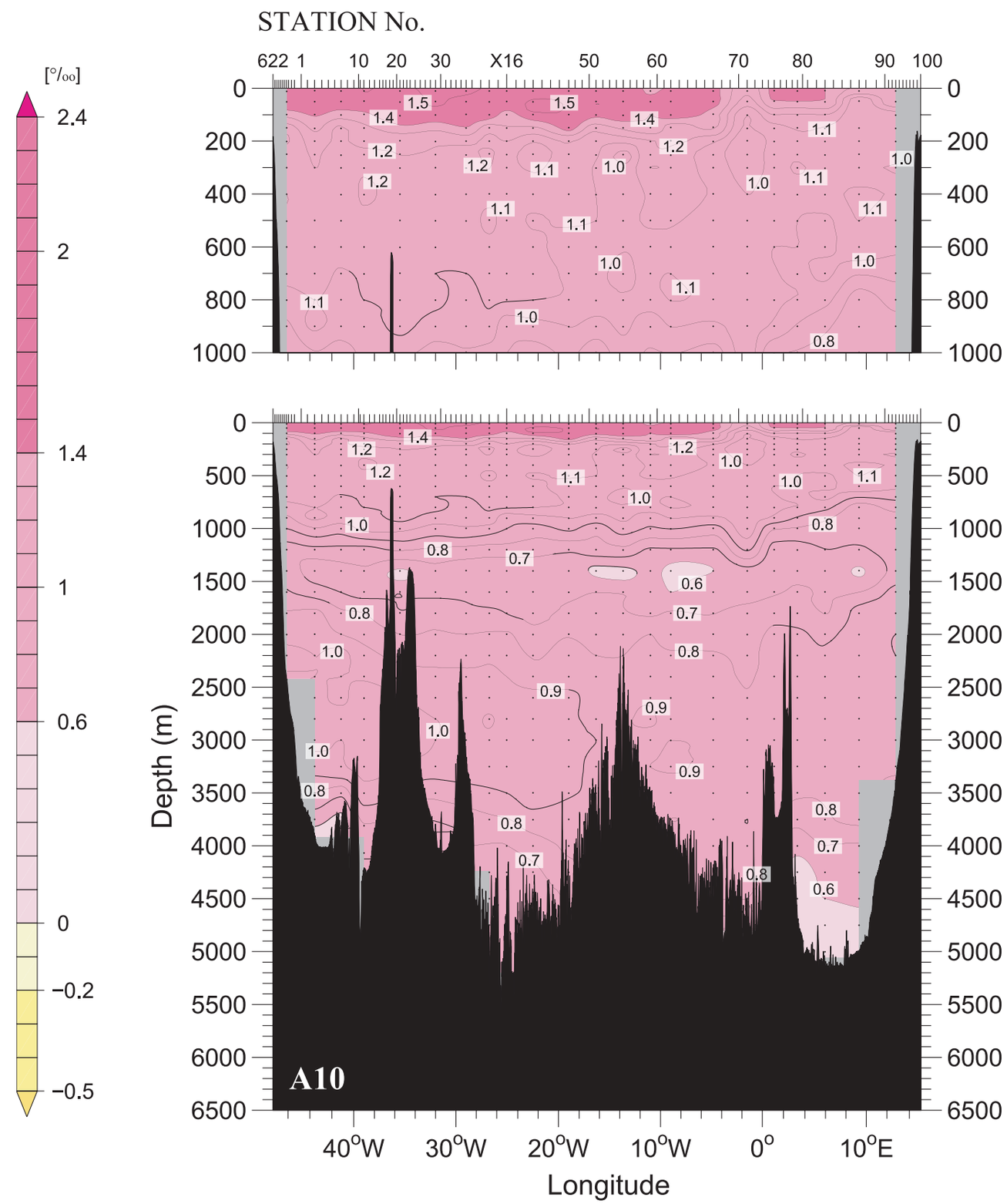
160°E 170°E 180° 170°W 160°W 150°W 140°W 130°W 120°W 110°W 100°W 90°W 80°W

Longitude

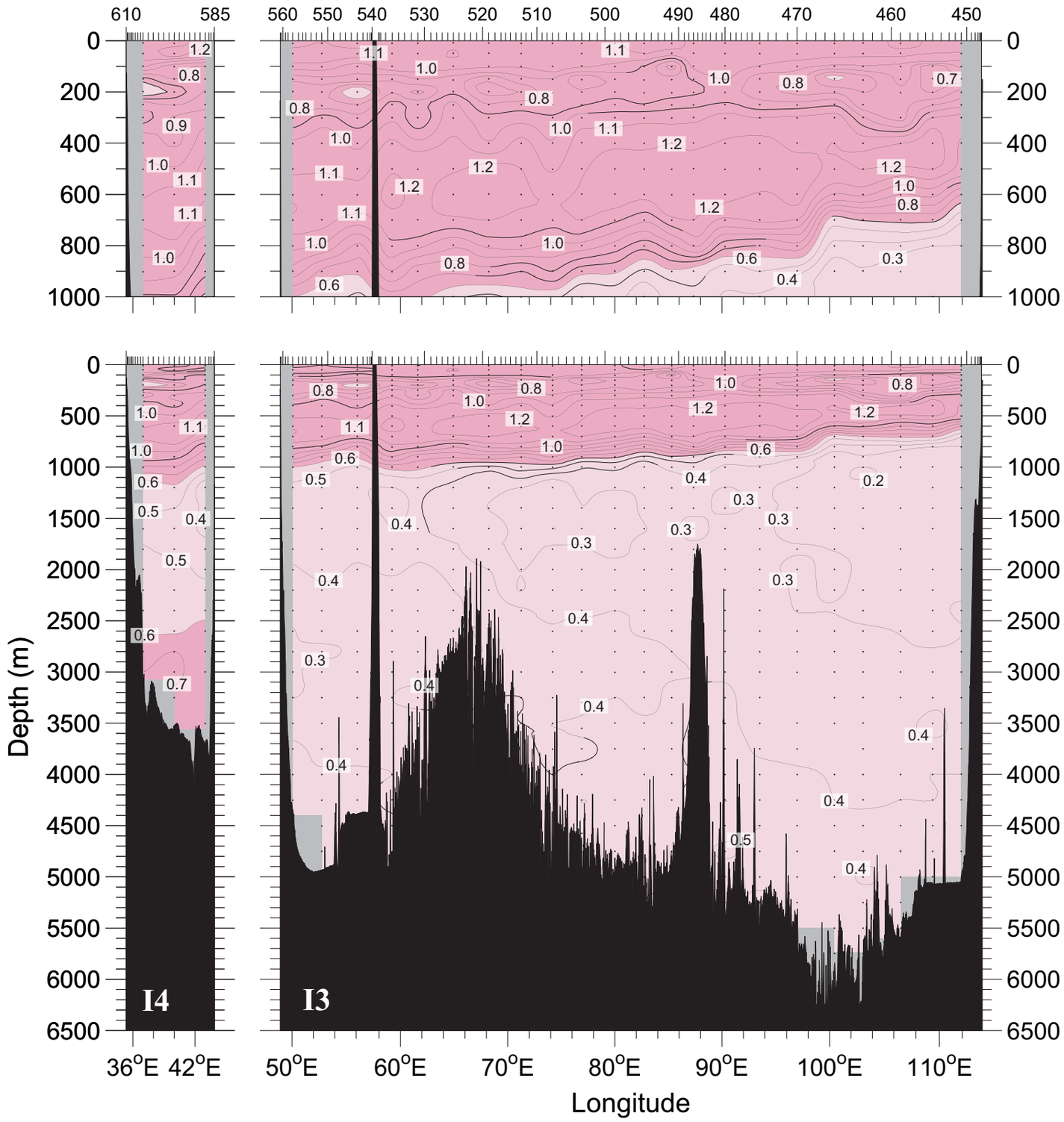
P6

**Figure 6**

**$\Delta^{13}C$ [‰]**



STATION No.


610
585
560
550
540
530
520
510
500
490
480
470
460
450
I4
I3
Depth (m)
Longitude
36°E
42°E
50°E
60°E
70°E
80°E
90°E
100°E
110°E

STATION No.

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

Depth (m)

0 200 400 600 800 1000 1500 2000 2500 3000 3500 4000 4500 5000 5500 6000 6500

160°E 170°E 180° 170°W 160°W 150°W 140°W 130°W 120°W 110°W 100°W 90°W 80°W

Longitude

P6