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

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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 MR05-05 cruise, named WHP-P03 Revisit Cruise, we collected seawater samples for $\delta^{13}C$ and $\Delta^{14}C$ analyses at stations along the WHP-P03 line (24°N approximately) in the North Pacific. Here we report the final results of $\delta^{13}C$ and $\Delta^{14}C$ of DIC. Our preliminary report of $\delta^{13}C$ and $\Delta^{14}C$ measurements is replaced by this final report. General information and other hydrographic data of the cruise have already published in our data book for WHP-P03 Revisit Cruise (Kawano and Uchida, 2007)

(3) Sample collection

The sampling stations are summarized in Figure 3.10.1 and Table 3.10.1. A total of 794 seawater samples, including 44 replicate samples, were collected between surface (about 10 m depth) and near bottom at 23 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 two times. Immediately after sampling, 10 cm^3 of seawater was removed from the bottle and poisoned by 50 μl of saturated $HgCl_2$

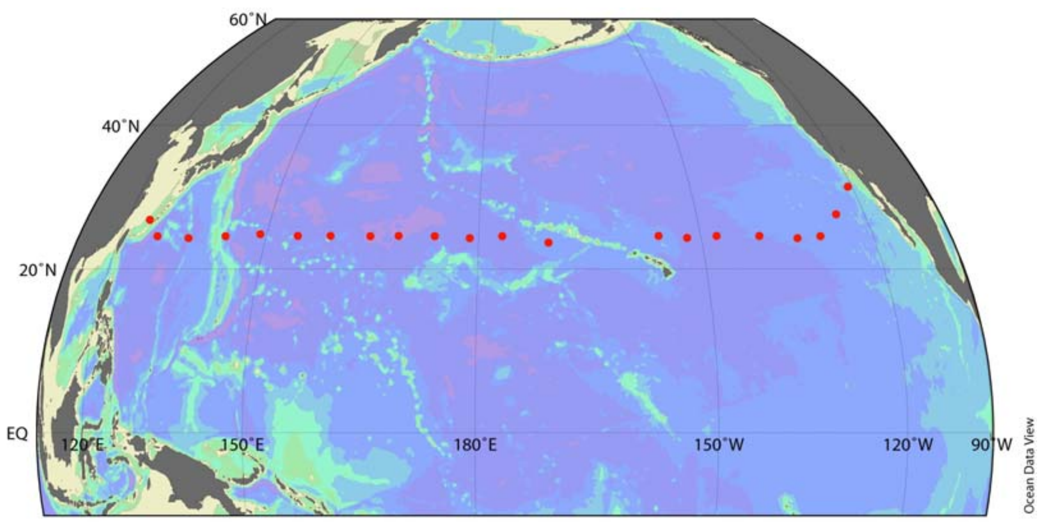

Figure 3.10.1 Sampling stations for $\delta^{13}C$ and $\Delta^{14}C$ of dissolved inorganic carbon during MR05-05 cruise (October, 2005–January, 2006) except stations 126 and 138.

Table 3.10.1 The sampling stations, number of samples, and maximum sampling pressure for carbon isotopes in DIC during MR05-05 cruise.

Station	No. samples	No. replicate samples	Max. sampling pressure /db
P03-024	28	2	4007.5
P03-038	30	2	4403.0
P03-051	31	2	4820.6
P03-X17	32	2	4927.2
P03-074	33	2	5066.1
P03-090	35	2	5666.1
P03-X16	34	2	5531.8
P03-114	31	2	4602.3
P03-126	33	2	5161.0
P03-138	32	2	4956.0
P03-173	31	2	4742.4
P03-189	34	2	5431.3
P03-X14	35	2	5836.6
P03-211	36	2	5827.9
P03-223	36	1	6242.2
P03-233	36	2	6076.8
P03-247	35	2	5602.4
P03-259	35	2	5675.4
P03-X10	36	2	5865.6
P03-293	36	2	6505.3
P03-X09	29	2	4165.6
P03-341	31	2	4596.0
P03-376	21	1	1911.4
Total	750	44	

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 µmol), ^{13}C measurement (about 100 µmol), and archive (about 200 µmol). 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 about 80 % in average by weighing of sample graphite powder. Details of these preparation procedures were described by Kumamoto et al. (2000).

$\delta^{13}C$ in the sample CO_2 gas was measured by a method in the following section just after the stripping. We found anomalous values of the isotopic ratio in samples from stations 126 and 138 in the central North Pacific and not from the other stations. Although causes of the anomalies were not confirmed, we probably forgot to add the $HgCl_2$ solution into the sample bottles during the sample collection at the two stations. Therefore we abandoned $\Delta^{14}C$ measurements for the samples from the two stations.

(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 -3.67 ‰ (Lot No. SHO-1250C) versus VPDB (Vienna Pee Dee Belemnite) standards. 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, National Electrostatic Corporation) and Japan Atomic Energy Agency in Mutsu (Model 4130-AMS, High Voltage Engineering Europa), 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 3.2 ‰ that correspond to repeatability of our $\delta^{13}C$ and $\Delta^{14}C$ measurements.

(6) Replicate measurements

Replicate samples were taken at all the stations. Results of 40 pairs of the replicate samples are shown in Table 3.10.2. The standard deviation of the $\delta^{13}C$ and $\Delta^{14}C$ replicate analyses was calculated to be 0.012 ‰ (n = 34) and 3.7 ‰ (n = 40), respectively. These were larger than the repeatability obtained from the individual measurements (0.004 ‰ for $\delta^{13}C$ and 3.2 ‰ for $\Delta^{14}C$) probably due to errors from sample preparation. We concluded that the precision of our $\delta^{13}C$ and $\Delta^{14}C$ analyses including error due to the sample preparation were about 0.01 ‰ and 4 ‰, respectively.

Table 3.10.2 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]
P03-024	32	-0.123	0.004	-0.165	0.037	19.6	3.2	19.3	2.3
		-0.176	0.002			19.0	3.2		
P03-024	13	-0.068	0.004	-0.054	0.011	-239.6	2.6	-235.4	5.9
		-0.053	0.001			-231.2	2.6		
P03-038	32	0.646	0.003	0.650	0.008	55.5	3.3	53.9	3.1
		0.658	0.004			51.1	4.4		
P03-038	13	-	-	-	-	-236.1	2.5	-234.2	2.7
		-	-			-232.3	2.5		
P03-051	32	0.740	0.002	0.736	0.013	63.0	3.5	63.8	2.4
		0.722	0.004			64.5	3.3		
P03-051	13	-0.022	0.003	-0.033	0.011	-232.7	2.7	-232.5	1.9
		-0.038	0.002			-232.3	2.7		
P03-X17	32	0.732	0.002	0.735	0.013	72.8	3.5	71.0	2.5
		0.751	0.005			69.2	3.5		
P03-X17	13	-0.041	0.004	-0.032	0.013	-229.5	2.7	-229.4	1.9
		-0.022	0.004			-229.2	2.7		
P03-074	32	-	-	-	-	78.9	3.7	77.9	2.6
		-	-			77.0	3.6		
P03-074	13	-0.072	0.001	-0.073	0.024	-239.7	2.7	-240.4	1.9
		-0.106	0.005			-241.1	2.8		
P03-090	32	0.664	0.005	0.661	0.004	80.9	3.8	84.0	4.3
		0.659	0.004			87.0	3.7		

Table 3.10.2 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]
P03-090	13	-0.017	0.003	-0.009	0.011	-242.3	3.0	-238.5	5.4
		-0.001	0.003			-234.6	3.0		
P03-X16	32	0.752	0.004	0.743	0.016	73.2	3.8	76.7	4.9
		0.730	0.005			80.1	3.7		
P03-X16	13	-0.109	0.003	-0.105	0.006	-241.2	2.7	-241.0	1.9
		-0.101	0.003			-240.7	2.8		
P03-114	32	0.680	0.004	0.684	0.005	92.5	3.7	87.1	7.8
		0.687	0.003			81.5	3.8		
P03-114	13	-0.012	0.004	-0.022	0.014	-230.2	2.8	-230.2	2.1
		-0.032	0.004			-230.3	3.1		
P03-173	32	0.728	0.006	0.722	0.004	67.7	3.5	71.0	4.9
		0.722	0.001			74.6	3.6		
P03-173	13	-0.042	0.003	-0.036	0.006	-232.8	2.9	-235.4	3.6
		-0.034	0.002			-237.9	2.8		
P03-189	32	-	-	-	-	72.1	3.3	74.2	3.0
		-	-			76.3	3.3		
P03-189	13	0.010	0.003	0.015	0.005	-230.2	2.7	-227.7	3.5
		0.017	0.002			-225.2	2.7		
P03-X14	32	0.715	0.004	0.716	0.003	74.8	7.2	76.4	5.1
		0.716	0.004			77.9	7.2		
P03-X14	13	0.000	0.003	-0.004	0.008	-229.3	5.3	-230.9	3.8
		-0.012	0.004			-232.6	5.4		
P03-211	32	0.643	0.002	0.643	0.002	82.3	3.5	81.3	2.4
		0.641	0.006			80.4	3.3		
P03-211	13	0.045	0.005	0.051	0.006	-227.1	2.6	-232.6	8.1
		0.053	0.003			-238.6	2.7		
P03-223	32	0.616	0.003	0.611	0.008	78.4	3.3	78.7	2.3
		0.605	0.003			78.9	3.3		
P03-223	13	0.035	0.003	0.035	0.003	-231.0	2.5	-227.9	4.5
		0.032	0.007			-224.7	2.5		

Table 3.10.2 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]
P03-233	13	0.054	0.005	0.050	0.004	-228.7	2.5	-226.0	3.8
		0.048	0.003			-223.3	2.5		
P03-247	32	0.637	0.003	0.645	0.011	87.3	3.3	86.5	2.4
		0.652	0.003			85.5	3.5		
P03-247	13	0.056	0.003	0.039	0.017	-230.6	2.5	-229.2	2.2
		0.032	0.002			-227.5	2.7		
P03-259	32	0.571	0.004	0.575	0.008	88.9	3.2	89.7	2.3
		0.582	0.005			90.5	3.2		
P03-259	13	0.063	0.004	0.065	0.002	-223.7	2.7	-219.4	6.6
		0.066	0.003			-214.4	2.9		
P03-X10	32	0.622	0.004	0.631	0.008	90.2	3.5	86.3	5.2
		0.633	0.002			82.8	3.3		
P03-X10	13	0.075	0.003	0.075	0.002	-220.0	2.7	-219.4	1.9
		0.075	0.004			-218.7	2.8		
P03-293	32	-	-	-	-	75.8	3.4	81.2	7.4
		-	-			86.3	3.3		
P03-293	13	0.042	0.004	0.044	0.002	-214.3	2.6	-216.0	2.5
		0.045	0.003			-217.8	2.7		
P03-X09	32	0.636	0.005	0.610	0.025	91.7	3.4	92.3	2.4
		0.600	0.003			92.8	3.4		
P03-X09	13	-	-	-	-	-220.7	2.8	-224.9	5.5
		-	-			-228.5	2.6		
P03-341	32	0.564	0.002	0.563	0.003	92.0	5.3	93.4	3.7
		0.560	0.004			94.8	5.3		
P03-341	13	-	-	-	-	-221.3	4.1	-223.6	3.3
		-	-			-225.9	4.1		
P03-376	32	0.610	0.003	0.609	0.002	78.1	3.4	80.0	2.7
		0.607	0.003			81.9	3.4		

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) Reference seawater measurements

During the sample measurements period from April 2007 to July 2008, 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 an open ocean. The surface seawater was filtered, exposed to ultraviolet irradiation, poisoned by $HgCl_2$, dispensed in 250 cm^3 glass bottles, and then has been stored since July 2004. The $\delta^{13}C$ and $\Delta^{14}C$ of the reference seawater was measured at every station series. The results are shown in Table 3.10.3. The standard deviations (n = 21) of $\delta^{13}C$ and $\Delta^{14}C$ were 0.028 ‰ and 7.0 ‰, respectively. These are larger than the precision (0.012 ‰ for $\delta^{13}C$ and 3.7 ‰ for $\Delta^{14}C$) obtained from the replicate measurements probably due to errors from the sample storage.

Table 3.10.3 Summary of reference seawaters (RS) 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	RM0407-130	25-Apr-07	-0.923	0.002	03-Sep-07	36.0	3.2
2	RM0407-058	14-May-07	-0.872	0.003	03-Sep-07	36.2	3.2
3	RM0407-037	15-May-07	-0.896	0.002	06-Sep-07	34.1	3.3
4	RM0407-117	18-May-07	-0.875	0.001	05-Dec-07	36.1	3.5
5	RM0407-038	11-Jun-07	-0.878	0.003	05-Dec-07	45.5	3.4
6	RM0407-166	12-Jun-07	-0.892	0.003	07-Jan-08	47.3	3.5
7	RM0407-140	14-Jun-07	-0.897	0.005	07-Jan-08	41.6	3.5
8	RM0407-094	03-Sep-07	-0.992	0.005	07-Jan-08	33.5	3.6
9	RM0407-009	10-Sep-07	-0.885	0.002	18-Feb-08	32.6	3.4
10	RM0407-067	08-Nov-07	-0.895	0.004	18-Feb-08	31.4	3.3
11	RM0407-127	15-Jan-08	-0.887	0.005	12-Mar-08	12.5	6.8
12	RM0407-113	18-Jan-08	-0.878	0.002	16-Jun-08	33.0	3.2
13	RM0407-059	22-Jan-08	-0.885	0.003	16-Jun-08	31.3	3.2
14	RM0407-133	23-Jan-08	-0.954	0.003	17-Jun-08	41.9	3.1
15	RM0407-001	13-Mar-08	-0.883	0.002	14-Jul-08	39.6	3.3
16	RM0407-114	25-Mar-08	-0.898	0.005	14-Jul-08	41.1	3.2
17	RM0407-150	26-Mar-08	-0.896	0.003	14-Jul-08	33.0	3.1
18	RM0407-088	10-Apr-08	-0.904	0.002	14-Jul-08	35.2	3.0
19	RM0407-186	21-Apr-08	-0.911	0.003	17-Jul-08	31.5	3.2
20	RM0407-139	20-Nov-07	-0.897	0.004	20-May-08	33.6	5.1
21	RM0407-146	22-Apr-08	-0.911	0.002	17-Jul-08	34.1	3.1

a. Decay corrected for 01/January/2009.
b. Standard deviation of repeat measurements.

c. Larger of the standard deviation and the counting error.

(8) 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 3.10.4). 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, 2008). If a datum was anomalous on the section plots, datum flag was degraded from 2 to 3, or from 3 to 4.

Quality flags of $\delta^{13}C$ and $\Delta^{14}C$ for all the samples from stations 126 and 138 (65 samples) are assigned to be 4 and 5, respectively.

Table 3.10.4 Summary of assigned quality control flags.

Flag	Definition	Number	
		$\delta^{13}C$	$\Delta^{14}C$
2	Good	639	636
3	Questionable	11	7
4	Bad	66	2
5	Not report (missing)	0	65
6	Replicate	34	40
Total		750	750

(9) Data Summary

Figure 3.10.2 shows vertical section of $\delta^{13}C$ against depth. Higher $\delta^{13}C$ values were observed in surface waters. Higher values were found in the eastern subtropical region. Minimum of $\delta^{13}C$ was found in deep waters from 500 to 2,000 m depth approximately and the smallest value was in the deep waters at the easternmost station. From the deep waters to the bottom $\delta^{13}C$ increases gradually. The general distribution of $\delta^{13}C$ well agrees with that presented in a previous study (Kroopnick, 1985) and is mainly governed by biogeochemical process and ocean circulation.

Figure 3.10.3 shows vertical section of $\Delta^{14}C$ against depth. Higher $\Delta^{14}C$ values were observed in the thermocline (< about 1,000 m depth) because of the bomb-produced radiocarbon penetration. Relative higher $\Delta^{14}C$ was measured below 4,000 m depth approximately where the high-$\delta^{13}C$ water was found.

Minimum of $\Delta^{14}C$ was found in deep waters from 1,500 to 4,000 m depth approximately and the smallest value was in the deep waters in the east of 140°W. The general distribution of $\Delta^{14}C$ in deep and bottom waters supports a previous study (Key et al., 2004) and indicates the global pattern of thermohaline circulation.

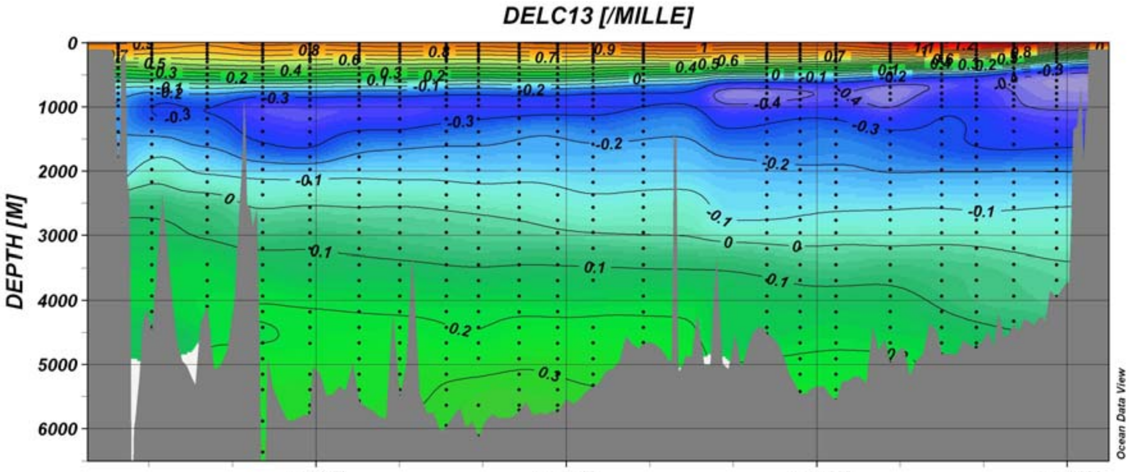

Figure 3.10.2 Vertical sections of $\delta^{13}C$ (‰) against depth along the WHP-P03 line in 2005/2006.

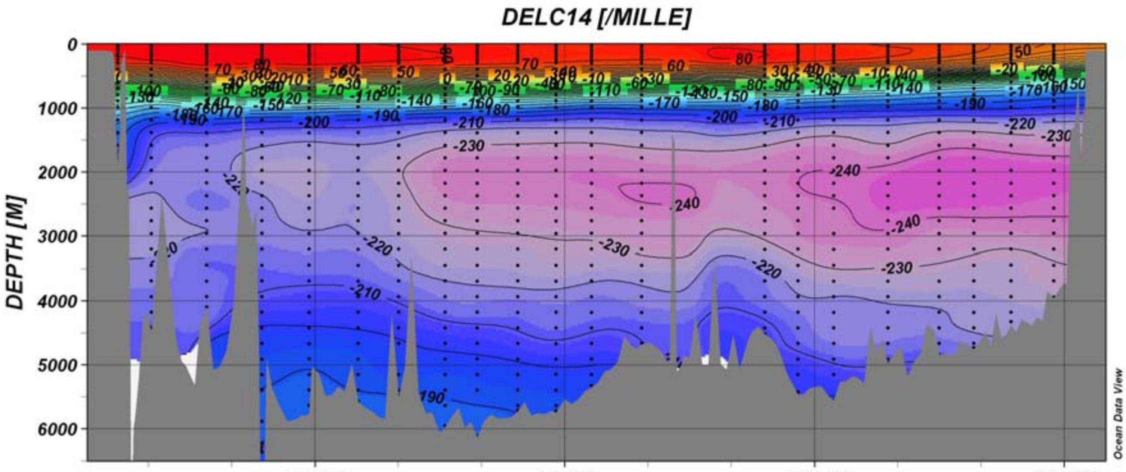

Figure 3.10.3 Vertical sections of $\Delta^{14}C$ (‰) against depth along the WHP-P03 line in 2005/2006.

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