

DISSOLVED INORGANIC RADIOCARBON IN THE NORTHWEST PACIFIC CONTINENTAL MARGIN

Tiantian Ge¹ • Xuchen Wang^{1,2*} • Jing Zhang³ • Chunle Luo¹ • Yuejun Xue¹

¹Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China.

²Qingdao Collaborative Innovation Center of Marine Science and Technology, Qingdao 266100, China.

³Graduate School of Science and Engineering, Toyama University, Toyama 9308555, Japan.

ABSTRACT. This article presents a modified method for extraction of dissolved inorganic carbon (DIC) from seawater for radiocarbon measurement by accelerator mass spectrometry (AMS). Standard tests indicate that the extraction efficiencies of DIC are >96%, and the respective precisions of $\Delta^{14}\text{C}$ -DIC and $\delta^{13}\text{C}$ -DIC analyses are 6‰ and 0.1‰ or better. Using the method, we report $\Delta^{14}\text{C}$ -DIC profiles collected from the shelf and slope in the East China Sea (ECS) of the northwest Pacific Ocean. Both the DIC concentration and $\Delta^{14}\text{C}$ -DIC in the shelf and slope regions seem primarily affected by the Kuroshio Current. It is estimated that 54–65% of the bottom water in the shelf region could be from the intrusion of Kuroshio intermediate water, which carries a high concentration and low $\Delta^{14}\text{C}$ values of DIC, and which influenced the DIC and its ^{14}C signature on the shelf. Compared with the $\Delta^{14}\text{C}$ -DIC profiles at other sites in the northwest Pacific reported previously, it appears that the $\Delta^{14}\text{C}$ -DIC distributions are mainly controlled by the major oceanic currents in the region, and large variations in $\Delta^{14}\text{C}$ -DIC occurred mostly in the upper 800 m of the water column. The similarity of $\Delta^{14}\text{C}$ -DIC at depth suggests that the deep-water circulation patterns have been relatively stable in the northwest Pacific Ocean in the last 20 yr.

KEYWORDS: dissolved inorganic carbon, radiocarbon, stable carbon isotope, East China Sea, continental margin.

INTRODUCTION

Dissolved inorganic carbon (DIC) in the ocean represents one of the largest exchangeable carbon pools on Earth, and it is directly linked to oceanic organic carbon production and cycling. The ocean is the major sink of atmospheric CO_2 ; about one-third of the anthropogenic CO_2 produced each year is absorbed by the ocean through air-sea exchange and dissolved as DIC in the ocean (Gruber et al. 2009). The distribution and cycling of DIC in the ocean, therefore, play crucial roles in the global carbon cycle and climate change (McKinley et al. 2006; Valsala et al. 2012; Yasunaka et al. 2014).

Measurement of radiocarbon abundances of DIC in the ocean is a powerful technique for studying the carbon cycle, water mass transport, and circulation timescales in the ocean (Key et al. 1996; Druffel et al. 2008; Santos et al. 2011). During the World Ocean Circulation Experiment (WOCE) Program and the ongoing Climate Variability and Predictability Program (CLIVAR), a large number of DIC samples have been collected from the world oceans and their $\Delta^{14}\text{C}$ compositions have been measured (Stuiver et al. 1996; McNichol et al. 2000). Results from $\Delta^{14}\text{C}$ -DIC measurements have provided great insight into our understanding of the oceanic carbon cycle and ocean circulation processes, as linked to climate variability (Stuiver et al. 1983; Druffel et al. 1989, 2008; Broecker et al. 1995; Key 1996).

Several methods have been developed to extract DIC from natural waters for high-precision ^{14}C analysis by accelerator mass spectrometry (AMS). The most commonly used method in many ^{14}C laboratories for DIC study is based on McNichol et al. (1994), which provides a relatively rapid and high-precision way to strip CO_2 from acidified seawater samples. More recently, Gao et al. (2014) developed a headspace method for extraction of seawater DIC for AMS ^{14}C analysis. This method requires much less water volume (30–40 mL) and no nitrogen gas stripping on a vacuum line is needed. Seawater is simply acidified in a 64-mL septum-sealed cap vial, and the CO_2 produced in the headspace can be collected using a gas-tight syringe and

*Corresponding author. Email: xuchenwang@ouc.edu.cn.

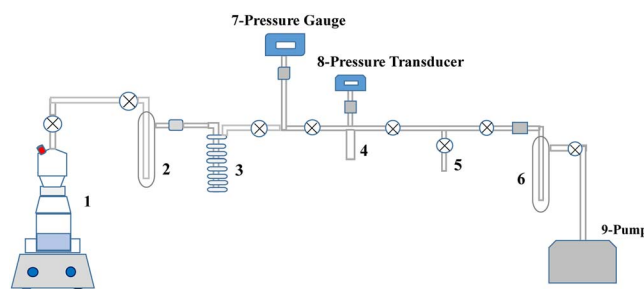


Figure 1 General scheme of the reaction and stripping probe (1) and the vacuum line system for DIC extraction from seawater.

further processed for ^{14}C analysis. The headspace method is very simple and rapid, but the extraction efficiency of DIC is rather low ($46.6 \pm 3.9\%$). In addition, a small isotopic fractionation of ^{13}C ($\leq 0.6\%$) also occurred due to the partial extraction of DIC (Gao et al. 2014). In many cases when quantitative determination of DIC concentrations in seawater is needed, this method has limitations.

This article reports a modified DIC extraction method based on McNichol et al. (1994). The method is relatively simple and effective and has been used in our laboratory to extract DIC from natural waters for ^{14}C analysis by AMS. Using the method, we report the first data set of ^{14}C values of DIC depth profiles collected in the shelf and slope of the East China Sea (ECS), one of the largest marginal seas in the northwest Pacific Ocean.

METHODS

Extraction of DIC

DIC was extracted from water samples as gaseous CO_2 and the extracted CO_2 was purified on a vacuum system. As shown in Figure 1, the vacuum line system includes a sample connection joint that can be connected with 100-mL borosilicate glass bottles with ground-glass-joint stripping probes (1); a cold (-80°C) water trap (2); a liquid nitrogen trap for freezing CO_2 (3); a vacuum gauge (7) (Agilent, 1×10^{-4} to 760 Torr) and a pressure transducer (8) (MKS, 0–1000 Torr); a calibrated volume cold-finger for CO_2 measurement and quantification (4); a CO_2 transport connection joint (5); and a liquid nitrogen protection trap (6) leading to an oil-free turbomolecular pump (9) (Agilent TPS Compact Dry TV301).

To test the extraction efficiency of the method and blank level of our new vacuum line, we used two inorganic materials with very different ^{14}C ages: (1) reagent-grade sodium carbonate standard and (2) a modern coral. A sodium carbonate standard was dissolved directly in preboiled and N_2 -bubbled Milli-QTM water (to remove dissolved CO_2) to make a 100-mM stock DIC solution. Based on the DIC concentration ranges measured in natural waters, we tested three concentrations: 1, 2, and 3 mM. Three precleaned 100-mL borosilicate glass bottles with ground-glass-joint stripping probes (Figure 1) were pumped down on the vacuum line to 10^{-3} Torr. In a N_2 -filled bag (to avoid contact with atmospheric CO_2), 50 mL of each standard DIC solution was injected into the glass bottle through a rubber septum-sealed tube on the top side of the probe using a syringe and a needle. Then, 1 mL of 85% H_3PO_4 acid was injected into the bottle to acidify the DIC sample to $\text{pH} \leq 2$. The glass bottles with acidified DIC samples were removed from the N_2 bag and placed in a hot water bath (70°C) for 30 min and shaken by

hand several times. At $\text{pH} \leq 2$, all the forms of DIC (carbonate, bicarbonate, and CO_2) dissolved in water will become CO_2 because the solubility of CO_2 in water is a function of temperature and pressure. Henry's law shows that at 70°C under vacuum, the solubility of CO_2 in water is $<6.0 \times 10^{-5} \mu\text{mol/L}$, so it is expected that all CO_2 dissolved in water escaped into the probe headspace. The glass bottle was removed from the hot water bath, cooled down for 5 min, then placed on a stir plate and attached at the top to the vacuum line. After evacuation, the stopcock on the top of the stripping probe was opened and the CO_2 generated was collected cryogenically into the liquid nitrogen trap. During this process, CO_2 was extracted under static vacuum conditions for 3 min and then pumped for 1 min to remove any uncondensed gases. It should be mentioned that since a considerable amount of water will be vacuumed out, an efficient cold (-80°C) water trap is necessary or adding second cold water trap to avoid a small amount of water carried into the liquid nitrogen trap. Usually, we clean and dry the water trap after processing every five samples. After the volume was measured and recorded, the CO_2 was flame-sealed inside 6-mm-outer-diameter PyrexTM tubes for ^{14}C and ^{13}C analysis. The whole process takes <15 min for each sample.

We also used modern coral (growing <30 yr) to test the extraction efficiency and vacuum line blank. The coral was first cleaned and ground. Then, 5-, 10-, and 15-mg particles of coral were weighed into three 100-mL borosilicate glass bottles and then connected to the ground-glass-joint stripping probes. The bottles were then pumped down on the vacuum line to 10^{-3} Torr, and 50 mL of preboiled and N_2 -bubbled Milli-Q water was injected into each bottle. After injecting 1 mL of 85% H_3PO_4 acid, the reaction bottles were placed in a 70°C hot water bath for 30 min. DIC produced from the dissolution of coral was extracted as CO_2 and collected on the vacuum line as described earlier.

Extraction of DIC from Seawater

DIC water profile samples were collected from the shelf and slope of the East China Sea (ECS) at six stations during a cruise in July 2014 on the Japanese Research Vessel (R/V) *Shinset Maru* (Figure 2). The ECS is one of the largest marginal seas on the northwest Pacific with a contiguous shelf area of about $0.75 \times 10^6 \text{ km}^2$. Many oceanographic processes of the ECS are strongly influenced by the Changjiang (Yangtze) River, the largest river in China and third largest river in the world (Milliman and Meade 1983). In addition, the shelf break region of the ECS receives a major influence from the upwelled subsurface water of the northward-flowing Kuroshio Current, providing major nutrient supplies to the region (Li 1994; Guo et al. 2006). For DIC water collection, we used the protocol described in McNichol and Jones (1991). Water was collected (after overflowing ~ 100 mL) in prebaked 100-mL glass bottles with ground-glass stoppers using precleaned silicone tubing connected directly to the Niskin bottle. After adding $50 \mu\text{L}$ of saturated HgCl_2 solution, the bottles were capped tightly with grease-coated ground-glass stoppers and secured with rubber bands to make a gas-tight seal. In the laboratory, the extraction procedure is the same as described earlier. In a N_2 -filled bag, 50 mL of water sample was injected into a pre-evacuated 100-mL borosilicate glass bottle with ground-glass-joint stripping probes. After injecting 1 mL of 85% H_3PO_4 , the glass bottle was placed in a 70°C hot water bath for 30 min and DIC was extracted as CO_2 and collected on the vacuum line as described.

Concentration of DIC Analysis

To determine the extraction efficiency, we measured DIC concentrations before and after extraction for all standard DIC solutions. The concentrations of DIC water profiles were

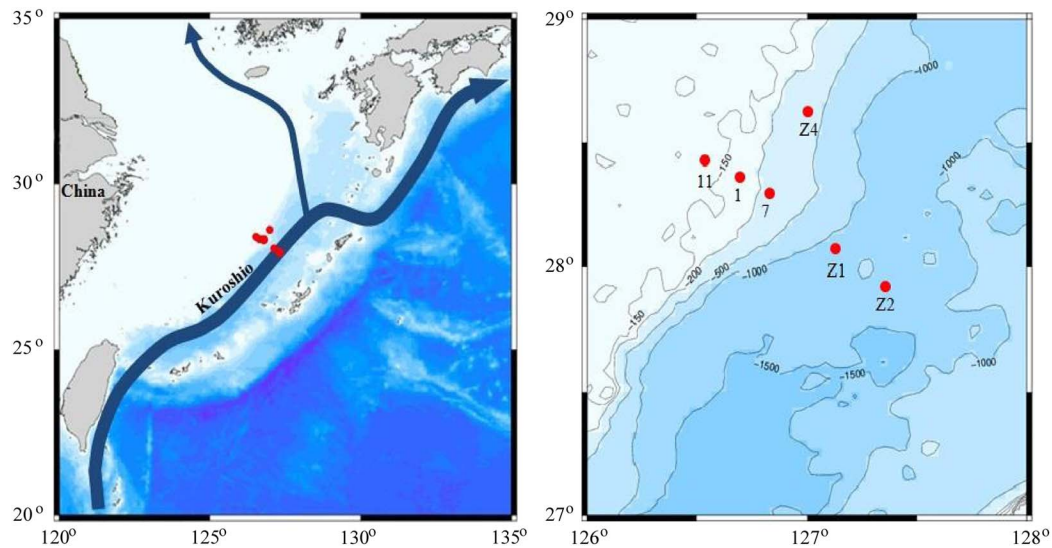


Figure 2 Map showing the water sampling stations in the shelf and slope regions in the East China Sea of the northwest Pacific during the cruise in July 2014. The region is influenced largely by the northward-flowing Kuroshio Current.

also measured. DIC was measured using a Shimadzu TOC-L analyzer equipped with an ASI-V autosampler, using the total inorganic carbon (IC) mode. The concentration of DIC was calibrated using a 5-point calibration curve prepared from reagent-grade sodium carbonate and sodium bicarbonate dissolved in DIC-free Milli-Q water as the IC standard. The instrument blank and DIC values were checked against DIC reference material (CRMs, Scripps Institute of Oceanography, University of California San Diego). Total blanks associated with DIC measurements were less than $3\ \mu\text{M}$, which is about $<0.15\%$ of seawater DIC concentrations, and the analytic precisions on triplicate injections were $<3\%$.

Isotopic Measurement

Purified CO_2 gas samples were sent to the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility at Woods Hole Oceanographic Institution (WHOI) for ^{13}C and ^{14}C analysis. A small split fraction of CO_2 was measured for $\delta^{13}\text{C}$ using a VG isotope ratio mass spectrometer (IRMS) and the rest of the CO_2 was graphitized for $\Delta^{14}\text{C}$ analysis using AMS. Values of $\delta^{13}\text{C}$ are reported in ‰ relative to the VPDB standard and values of $\Delta^{14}\text{C}$ are reported as the modern fraction based on the modern reference material used (McNichol et al. 1994). The conventional ^{14}C ages (years before present, or yr BP) were calculated following Stuiver and Polach (1977).

RESULTS

Method Validation

Our modified method showed very good extraction efficiency and high precision of both ^{13}C and ^{14}C measurements as compared to the standard materials (Table 1). The results indicate that the extraction efficiencies are in the range of 96–98% for the DIC solutions tested. The differences of measured average values of $\delta^{13}\text{C}$ (-5.17% , $1\sigma = 0.01$) and $\Delta^{14}\text{C}$ (40.3% , $1\sigma = 3.2$) of extracted coral DIC are less than 2% and 4% compared to the values of the coral standard; the mean values are almost the same ($\delta^{13}\text{C} = 14.8\%$, $1\sigma = 0.10$; $\Delta^{14}\text{C} = 993\%$,

Table 1 Comparison of measured $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of coral standard and Na_2CO_3 standard and prepared DIC extracted using the method.

Sample	NOSAMS #	DIC (mM)	Recovery	Fraction modern	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)	^{14}C age (yr BP)
Coral Std-1	OS-112645			1.0495 ± 0.0024	-5.17	41.4	Modern
Coral Std-2	OS-112646			1.0505 ± 0.0029	-5.16	42.4	Modern
Na_2CO_3 Std	OS-112747			0.0056 ± 0.0010	-14.9	-994	41,000
Coral DIC	OS-117670	1.0	97%	1.0487 ± 0.0029	-5.27	40.6	Modern
Coral DIC	OS-117671	2.0	98%	1.0443 ± 0.0026	-5.26	36.3	Modern
Coral DIC	OS-117672	3.0	97%	1.0522 ± 0.0025	-5.28	44.1	Modern
Na_2CO_3 DIC	OS-117673	1.0	98%	0.0078 ± 0.0007	-14.8	-992	39,000
Na_2CO_3 DIC	OS-117699	2.0	96%	0.0061 ± 0.0003	-15.0	-994	41,000
Na_2CO_3 DIC	OS-117712	3.0	97%	0.0067 ± 0.0003	-15.0	-993	40,200

$1\sigma = 0.8$) between the extracted sodium carbonate DIC and the standard (Table 1), indicating that the blank effect from the vacuum line during extraction processing is very small. Compared to the traditional extraction method of McNichol et al. (1994), our modified method used water bath heating and eliminated the use of N_2 gas bubbling for stripping during extraction of CO_2 . The sample handling process is relatively simple and rapid. In our laboratory, we usually process 10 DIC samples a day.

DIC Concentration Profiles in the ECS

All hydrographic data and measurements are summarized in Table 2. The temperature ranged from 26.31 to 29.34 in the surface waters (5–10 m) and decreased with depth at all stations (Figure 3a). For the four shelf stations (1, 7, 11, and Z4), although their water depths are shallower, the temperature decreased more rapidly and the values were significantly lower than the two slope stations Z1 and Z2. The salinity ranged from 33.92 to 34.87 for the stations (Table 2). As plotted in Figure 3b, salinity was lower in the surface and increased with depth in the upper 100 m and then decreased for all stations. For Stations Z1 and Z2, the salinity values were identical below 600 m depth. A transectional distributions of sigma- t plot for the sampling stations (Figure 4) showed that the water mass in the sampling area is composed of mixed Kuroshio and ECS shelf waters. This is consistent with the salinity profiles of the stations as plotted in Figure 3b. The concentration profiles of DIC ranged from 1.777 to 2.045 mM/kg for the four shelf stations (Stations 1, 7, 11, and Z4), and from 1.720 to 2.142 mM/kg for the two deep slope stations (Z1 and Z2), respectively. As plotted in Figure 5a, DIC concentrations increased with depth for all stations (except 160 m at Station 1). In the surface water (<20 m), concentrations of DIC showed fewer variations (1.749 to 1.822 mM/kg) among the stations. DIC concentrations increased more rapidly with depth for the shelf stations compared with the slope stations (Z1 and Z2), and DIC was higher in the shelf water column (<420 m) than in the slope water column at the same depths (Figure 5a).

Carbon Isotopic Signatures of DIC in the ECS

Using our DIC extraction method, we processed 41 DIC samples collected from the shelf and slope of the ECS. The measured DIC $\Delta^{14}\text{C}$ values ranged from 42.5‰ to -55.6‰ for the shelf

Table 2 Hydrographic data, DIC concentration, and isotopic natural abundance in DIC for water samples collected from the NW Pacific margin in July 2014.

Station #	Depth (m)	Temp. (°C)	Salinity	DIC (mmol/kg)	$\Delta^{14}\text{C}$ (‰)	$\delta^{13}\text{C}$ (‰)
Station 11	5	26.31	33.92	1.777	31.0	0.14
28°25.92'N	20	25.45	33.95	1.821	30.2	0.10
126°31.96'E	60	23.58	34.21	1.841	29.6	0.08
	100	18.42	34.64	1.966	3.9	-1.10
	138	13.42	34.48	2.045	-42.0	-1.10
Station 1	5	27.51	33.96	1.805	12.3	-0.26
28°22.13'N	30	26.12	34.19	1.804	20.9	0.15
126°41.60'E	50	23.42	34.60	1.909	29.6	0.30
	140	14.11	34.48	1.923	19.6	0.10
	160	13.51	34.48	1.862	6.4	-0.60
Station 7	5	27.38	33.89	1.799	31.0	0.29
28°18.03'N	40	26.28	34.10	1.826	36.3	-0.05
126°49.99'E	80	21.97	34.58	1.888	42.5	-0.17
	180	17.23	34.67	1.897	30.1	0.29
	240	15.38	34.56	1.933	30.9	-0.44
Station Z4	5	28.03	34.12	1.760	21.0	0.69
28°38.06'N	60	25.07	34.64	1.766	5.0	0.45
127°00.00'E	120	20.04	34.69	1.971	1.6	-1.15
	240	12.57	34.44	1.962	-9.6	-0.50
	300	10.35	34.34	2.008	-12.8	0.03
	413	8.85	34.30	2.034	-55.6	-0.16
Station Z1	10	29.18	34.45	1.822	43.5	-0.09
28°04.41'N	25	28.02	34.5	1.828	38.0	0.25
127°07.80'E	90	25.20	34.80	1.793	34.2	0.20
	150	22.00	34.82	1.812	31.6	0.18
	200	19.20	34.77	1.889	25.3	0.08
	400	11.55	34.36	1.894	18.7	-0.90
	700	5.99	34.32	2.102	-102.4	-1.05
	800	5.24	34.35	2.098	-131.2	-0.06
	1000	4.21	34.40	2.111	-169.7	-0.35
	1100	4.09	34.41	2.127	-187.2	-0.82
Station Z2	10	29.34	34.48	1.749	31.1	0.60
27°55.67'N	50	27.87	34.45	1.720	33.9	0.68
127°21.34'E	90	24.23	34.82	1.801	31.4	0.19
	125	23.08	34.87	1.823	42.7	-0.33
	300	16.71	34.66	1.829	48.4	0.20
	500	10.19	34.32	1.942	-31.2	-0.57
	600	8.01	34.30	2.085	-86.1	-0.31
	800	5.31	34.34	2.111	-149.0	-0.56
	1000	4.29	34.39	2.142	-188.4	-1.16
	1295	3.87	34.42	2.086	-205.1	-1.1

stations and 48.4‰ to -205.1‰ for the slope stations. The depth profiles of $\Delta^{14}\text{C}$ -DIC showed an opposite trend to the concentrations of DIC. Higher DIC concentrations in the shelf stations 11 and Z4 had lower $\Delta^{14}\text{C}$ -DIC values (Figure 5b). In the surface waters (<20 m), values of $\Delta^{14}\text{C}$ showed fewer variations and then decreased with depth in general. At Stations 11 and Z4,

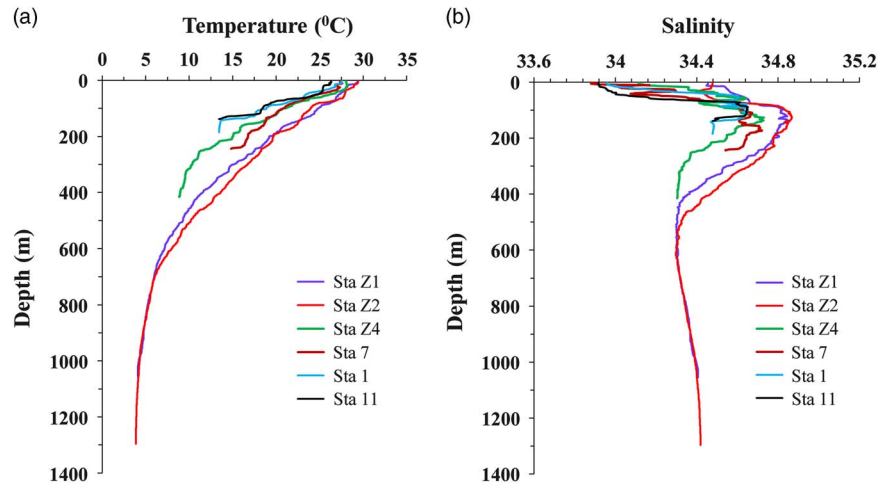


Figure 3 Depth profiles of temperature ($^{\circ}\text{C}$) and salinity (‰) for the six sampling stations in the East China Sea during the cruise in July 2014.

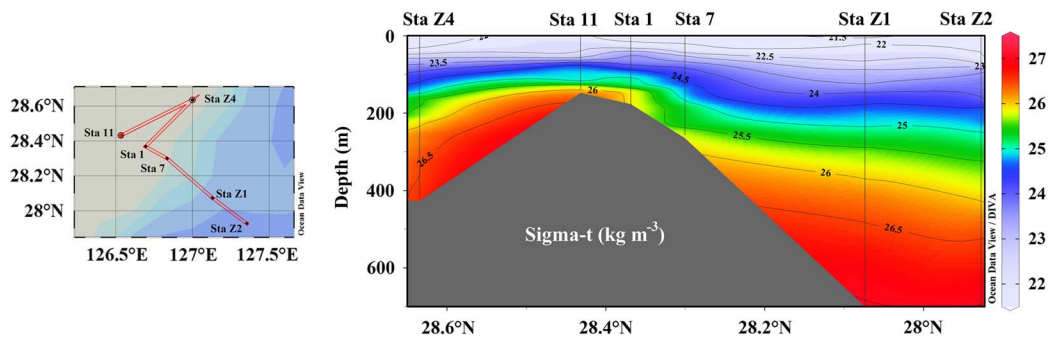


Figure 4 Transectional distribution of sigma- t (density 1000) for the sampling stations in the East China Sea during the cruise in July 2014.

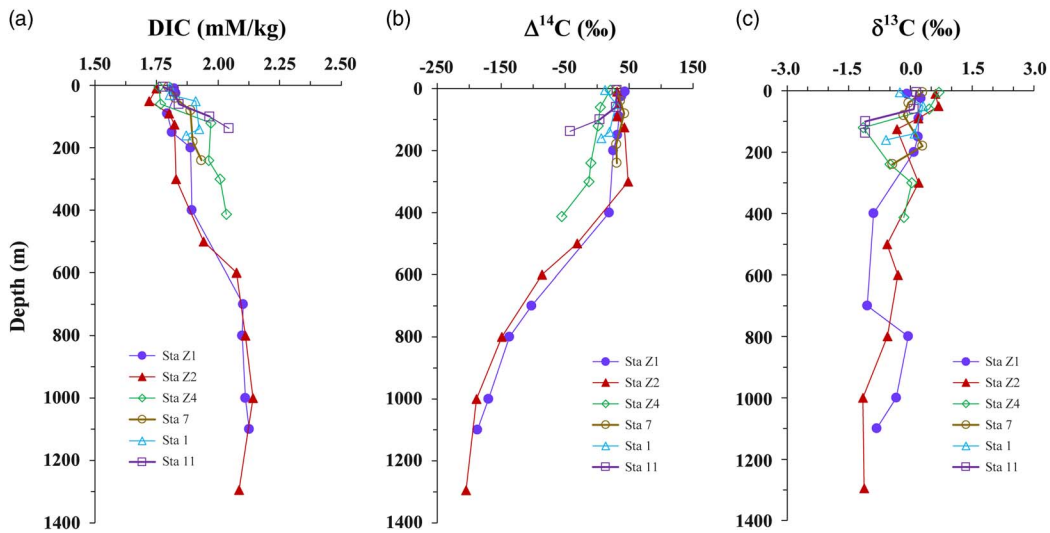


Figure 5 Depth profiles of DIC, $\Delta^{14}\text{C}$ -DIC, and $\delta^{13}\text{C}$ -DIC measured in the shelf and slope stations in the East China Sea

the $\Delta^{14}\text{C-DIC}$ values (3.9‰ to -55.6‰) at 100–413 m depth are significantly lower than the values of the slope stations Z1 and Z2 at the same water depth (18.7‰ to 48.4‰). Below 400 m depth, the $\Delta^{14}\text{C-DIC}$ values of Stations Z1 and Z2 are very similar and decreased with depth. Depth profiles of $\delta^{13}\text{C-DIC}$ are plotted in Figure 5c. Values of $\delta^{13}\text{C-DIC}$ ranged from 0.69‰ to -1.15‰ for the four shelf stations (1, 7, 11, and Z4) and from 0.68‰ to -1.16‰ for the two slope stations Z1 and Z2. It appears that no clear differences and trend exist for $\delta^{13}\text{C-DIC}$ between the shelf and slope stations.

DISCUSSION

Influence of Kuroshio on DIC in ECS

The ECS is one of the largest marginal seas in the northwest Pacific Ocean. Many oceanic processes and material transport in the inner shelf range of ECS are affected mostly by the input of Changjiang (Yangtze), the largest river in China and the second largest river in the world in terms of freshwater discharge (Milliman and Meade 1983). In the outer shelf and slope range of the ECS, it is affected largely by the northward-flowing Kuroshio Current (Delcroix and Murtugudde 2002; Lie et al. 2003; Kamidaira et al. 2014; Hu et al. 2015). The influence of the Kuroshio on the ECS is primarily associated with the nutrient-rich mid-depth water of the current that upwells into the slope and shelf ranges of the ECS (Qiu 2001; Andres et al. 2008; Bai and Zhang 2008). For the slope stations Z1 and Z2, it appears that the modern $\Delta^{14}\text{C-DIC}$ was well mixed in the top 400 m. The high DIC concentrations with the lower $\Delta^{14}\text{C-DIC}$ values observed in the shelf stations clearly indicate influence by different water masses with high DIC concentrations and low values of $\Delta^{14}\text{C-DIC}$ (Figures 5a, b). Although the Changjiang (Yangtze) River input plays an important role in affecting the ECS, these stations were not likely affected by freshwater input from the Changjiang (Yangtze) River because the salinity distributions in the shelf stations were high and quite uniform without any freshwater dilution signals. DIC concentrations in the Changjiang (Yangtze) River ranged from 1.38 to 1.73 mM/L and the riverine $\Delta^{14}\text{C-DIC}$ values were low, ranging from -156‰ to -137‰, as we measured during the low and high flood periods in 2014 (Wang et al. 2016). However, the DIC concentrations increased to 1.80–2.23 mM/L and $\Delta^{14}\text{C-DIC}$ increased to the modern values of -2.1‰ to 16.0‰ beyond the estuarine mixing at the river mouth. The modern $\Delta^{14}\text{C-DIC}$ values in the shelf waters of ECS are mainly controlled by air-sea mixing (Wang et al. 2016) and the $\Delta^{14}\text{C-DIC}$ values should be well mixed in the inner shelf because the water depth of the shelf range in the ECS is relatively shallow (<100 m, Figure 2). It is therefore impossible that the well-mixed shelf waters could bring low $\Delta^{14}\text{C-DIC}$ values to the bottom water depth at Stations 11 and Z4. Decomposition of ^{14}C -depleted dissolved organic carbon (DOC) in the shelf waters could contribute to the low $\Delta^{14}\text{C-DIC}$, but this effect is relatively small when comparing the DOC pool with the much bigger DIC pool in the ocean (Kashgarian and Tanaka 1991; Bauer et al. 1998; Druffel et al. 2008). In addition, sediment contributions might change $\Delta^{14}\text{C-DIC}$ values in the bottom water. Turbidity in the bottom water (413 m, Figure 6) is slightly higher than in the shallower water in Station Z4; however, it is very similar to that in Station 7 but without $\Delta^{14}\text{C-DIC}$ depletion, suggesting a minor sediment effect. Similarly, the turbidity profile in Station 11 is comparable with that of Station 1 (Figure 6), but it still cannot account for the ~50‰ $\Delta^{14}\text{C-DIC}$ difference caused by sediment impact between these two stations. We believe that this is likely evidence of intrusion of Kuroshio intermediate water (500–800 m) into the shelf range of the ECS. This intrusion more likely took place as upwelling of intermediate Kuroshio water along the bottom (Guo et al. 2006; Yang et al. 2011, 2012). The sigma- t diagram as showing in Figure 4 also provides clear evidence supporting the idea that the Kuroshio intermediate water upwells onto the ECS shelf and affected the bottom waters at

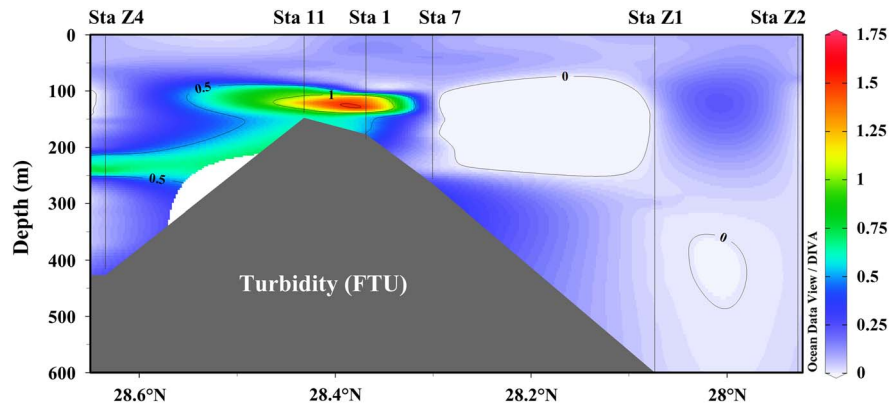


Figure 6 Transectional distribution of turbidity in the shelf and slope stations in the East China Sea.

Stations Z4 and 11 (Figure 4). It seems that this upwelling intrusion had almost no effect on the surface water (<100 m depth) for the shelf stations we sampled. However, we are not able to tell how far and how strongly this Kuroshio intrusion extended into the shelf range beyond Stations 11 and Z4. This intrusion we observed could reflect a smaller-scale or eddy effect rather than a large-scale Kuroshio intermediate water influence. If we use the average surface $\Delta^{14}\text{C}$ -DIC value of 26‰ measured at Stations 11 and Z4, and the average $\Delta^{14}\text{C}$ -DIC value of -100‰ for the intermediate Kuroshio water (500–800 m) as the end-member for the two water masses, we calculate that a contribution of about 54–65% Kuroshio intermediate water is required to produce the $\Delta^{14}\text{C}$ -DIC values observed in the bottom waters at Stations 11 and Z4. This result agrees well with the estimate by Bai and Zhang (2008) using rare earth elements that 30–40% of Kuroshio intermediate water supplies the outer-shelf bottom water (100–130 m depth).

Comparison of $\Delta^{14}\text{C}$ -DIC in the Northwest Pacific Ocean

A large number of DIC samples was collected for $\Delta^{14}\text{C}$ measurements in the northwest Pacific during the WOCE Program (Key 1996; McNichol et al. 2000). Stations P09-21 and P09-26 from the transection line P09 during the WOCE cruise 49RY9407 in 1994 (R/V *Ryofu Maru*) were nearby our Z1 and Z2 sites. As an attempt, we compared the $\Delta^{14}\text{C}$ -DIC values of Stations Z1 and Z2 with the results from Stations P09-21 and P09-26 measured 20 years ago (<http://cdiac.ornl.gov/ftp/oceans/p09woce/>) to see what changes have happened for $\Delta^{14}\text{C}$ -DIC in the region. As shown in Figure 7, we also compared the $\Delta^{14}\text{C}$ -DIC values reported for a subarctic station (NWP) by Tanaka et al. (2010). Both P09-21 and P09-26 were in the Kuroshio region. The NWP site $\Delta^{14}\text{C}$ -DIC profile was collected in 2006 (Tanaka et al. 2010) and it was in the eddy of the Western Subarctic Gyre region and influenced by the southward-flowing Oyashio (Figure 7). For our Station Z site, we used the average $\Delta^{14}\text{C}$ -DIC values of Stations Z1 and Z2 because the depth profiles are similar for these two stations (Figure 5b).

As shown in Figure 8, we plotted both salinity (Figure 8a) and $\Delta^{14}\text{C}$ -DIC (Figure 8b) profiles for the stations. Significant differences exist for both salinity and $\Delta^{14}\text{C}$ -DIC values in the top 1000 m depth at these sites. Salinity values at the NWP site were lower than the other stations in the upper 600 m depth, indicating the less-dense water mass carried by the Subarctic Current due to the observed cooling and freshening of the upper layer in the Oyashio and Sea of Okhotsk during the time (Rogachev 2000; Onishi 2001). At Station Z, $\Delta^{14}\text{C}$ -DIC values are

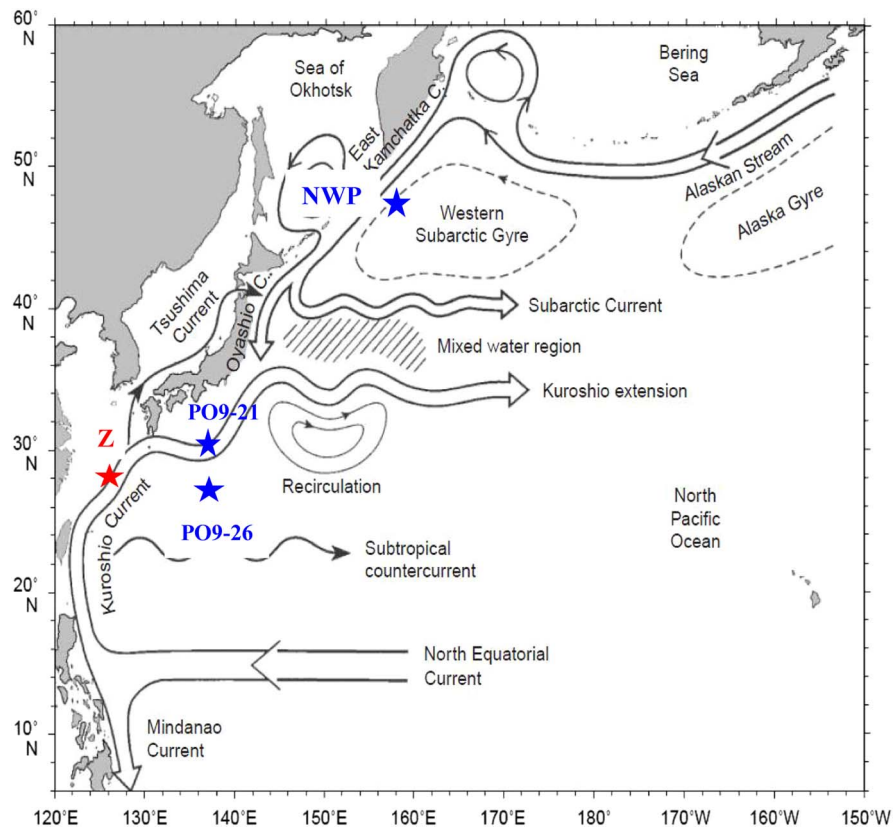


Figure 7 Map showing the major currents in the northwest Pacific and the four sites (Z, NWP, PO9-21, and PO9-26) for the comparison of $\Delta^{14}\text{C}$ -DIC depth profiles. The map is adopted from Qiu (2001). Stations PO9-21 and PO9-26 were the WOCE cruise 49RY9407 stations collected in 1994.

about 80‰ lower than the values at Stations PO9-21 and PO9-26 in the surface 200 m, and the differences decreased with depth from 400 to 1200 m (Figure 8b). Below 1000 m, the $\Delta^{14}\text{C}$ -DIC values are quite comparable at these sites. For the $\Delta^{14}\text{C}$ -DIC profile at the NWP site as reported by Tanaka et al. (2010), the values are about 180‰ to 250‰ lower than the values at sites PO9-21 and PO9-26 and about 80‰ to 150‰ lower than the values at site Z in the upper 400 m. The differences also decreased with water depth, and below 1200 m, the values became similar for the sites (Figure 8b).

The differences of $\Delta^{14}\text{C}$ -DIC values at these sites in the northwest Pacific reflect different processes affecting the $\Delta^{14}\text{C}$ signatures of DIC. Site Z and Stations PO9-21 and PO9-26 are all within the flow path of Kuroshio as the western boundary of the North Pacific Gyre (Qiu 2001; Hu et al. 2015). The $\Delta^{14}\text{C}$ -DIC at these three sites therefore should have similar values. Because the samples for PO9-21 and PO9-26 were collected in 1994 during the WOCE cruise, the difference in $\Delta^{14}\text{C}$ -DIC values at the PO9 and Z sites is likely due to the decrease of the bomb $\Delta^{14}\text{C}$ signal in the atmosphere in the last 20 years (from 1994 to 2014) that has mixed into the upper ocean through air-sea exchange. As reported by Levin and Hesshaimer (2000), the decrease of $\Delta^{14}\text{CO}_2$ in the atmosphere slowed down to about $-4\% \text{ yr}^{-1}$ in 1998. If the decrease rate stayed the same in the last 20 years, then an -80% decrease in $\Delta^{14}\text{CO}_2$ value would be

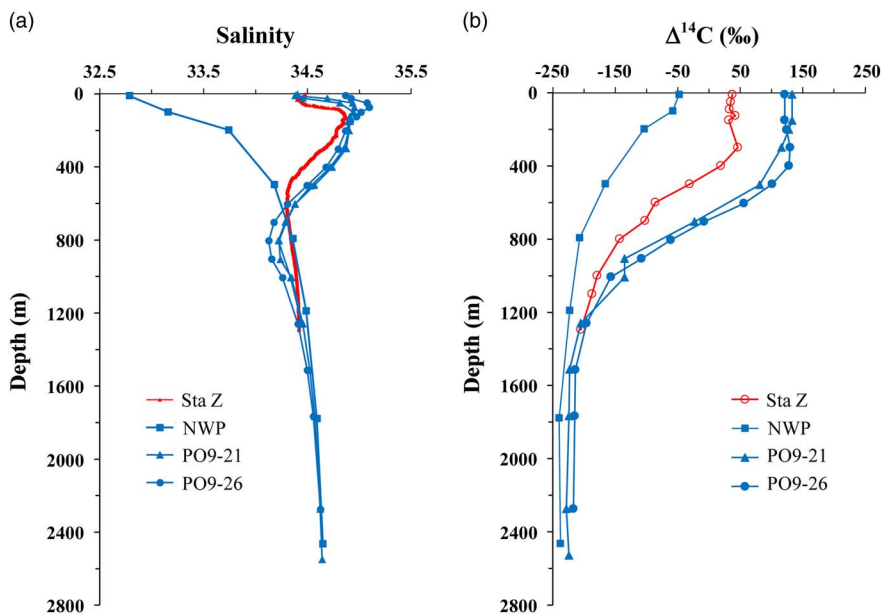


Figure 8 Depth profiles of (a) salinity and (b) $\Delta^{14}\text{C}$ -DIC in the Z and NWP sites and two WOCE Stations PO9-21 and PO9-26. Values for Station Z are the average values of Station Z1 and Z2 (collected in 2014). Values for NWP are from Tanaka et al. (2010) and the values for WOCE Stations PO9-21 and PO9-26 (collected in 1994) are downloaded from <http://cdiac.ornl.gov/ftp/oceans/p09woce/>.

expected today compared with 1994. This could explain the observed $\Delta^{14}\text{C}$ -DIC differences between Station Z and the PO9 sites (Figure 8b). For the NWP site, however, the observed $\Delta^{14}\text{C}$ -DIC differences could not be explained by changes of $\Delta^{14}\text{CO}_2$ in the atmosphere. They reflect the different water masses in the upper 1000 m at the two sites. As shown in Figure 7, the NWP site was influenced by the Oyashio Current, which flows southward and brings subarctic water to the surface and then mixes with the Kuroshio Current flowing eastward (Qiu 2001; Qiu and Chen 2011). The subarctic water with low $\Delta^{14}\text{C}$ -DIC values was clearly observed at the NWP site by Tanaka et al. (2010). The unchanged distributions of $\Delta^{14}\text{C}$ -DIC in the deep depths (1200 m below) at these stations (Figure 8b) suggest that the North Pacific Intermediate Water (NPIW) is still occupied by a similar water mass as transported by its global ocean circulation (Tsunogai et al. 1995) even though some chemical properties such as dissolved oxygen and nutrients showed some temporal and special variations in the northwest Pacific in the past (Tsurushima et al. 2002; Takatani et al. 2012). Currently, we are analyzing more DIC samples collected in the water mixing region of Oyashio and Kuroshio and its extension to reveal more detailed information about currents and water transport in the northwest Pacific Ocean.

SUMMARY

A modified DIC extraction method for ^{14}C measurement by AMS is presented. The method is operationally relatively simple and shows good extraction efficiency and reproducibility. The blanks associated with the method are low and precisions for both $\Delta^{14}\text{C}$ -DIC and $\delta^{13}\text{C}$ -DIC measurements are good. Using the method, we report the first data set of $\Delta^{14}\text{C}$ -DIC profiles in the shelf and slope waters of the ECS.

The depth profiles of both DIC concentration and $\Delta^{14}\text{C}$ -DIC in the shelf and slope regions of ECS are affected by the Kuroshio. It is estimated that 54–65% of the bottom water in the shelf region could be from the intrusion of Kuroshio intermediate water, which causes the high concentrations of DIC and low values of $\Delta^{14}\text{C}$ -DIC in the bottom water in the shelf region. As compared to the $\Delta^{14}\text{C}$ -DIC profiles in the WOCE PO9 stations and NWP sites, it appears that the $\Delta^{14}\text{C}$ -DIC values are largely controlled by the air-sea exchange of $^{14}\text{CO}_2$ in the atmosphere and the major oceanic currents in the northwest Pacific; the large variations in $\Delta^{14}\text{C}$ -DIC mainly occurred in the upper 800 m depth. The unchanged distributions of $\Delta^{14}\text{C}$ -DIC in the deep depths suggests that the deep-water circulation patterns have been relatively stable in the northwest Pacific Ocean in the last 20 years.

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