Insights into the coupling of upper ocean-benthic carbon dynamics in the western Arctic Ocean from an isotopic (^{13}C, ^{234}Th) perspective

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Abstract

The coupling of upper ocean-benthic carbon dynamics in the ice-free western Arctic Ocean (the Chukchi Sea and the Canada Basin) was evaluated during the late July–early September 2003 using natural stable (^{13}C) and radioactive (^{238}U-^{234}Th) isotope tracers. POC export flux estimated from ^{234}Th/^{238}U disequilibria and dissolved CO_2 concentration ($[CO_2(aq)]$) pointed out that the strengthened biological pump in the Chukchi Shelf have significantly lowered $[CO_2(aq)]$ and altered the magnitude of isotopic (^{12}C/^{13}C) fractionation during carbon fixation in the surface ocean. Further, δ^{13}C signatures of surface sediments ($\delta^{13}C_{sed}$) are positively correlated to those of weighted $\delta^{13}C_{POC}$ in upper ocean ($\delta^{13}C_{sed} = 13.64 + 1.56 \times \delta^{13}C_{POC}$, $r^2 = 0.73$, $p < 0.01$), suggesting that the POC isotopic signals from upper ocean have been recorded in the sediments, partly due to the rapid export of particles as evidenced by low residence times of the highly particle-reactive ^{234}Th from the upper water column. It is suggested that there probably exists an upper ocean-benthic coupling of carbon dynamics, which likely assures the sedimentary δ^{13}C record an indicator of paleo-CO_2 in the western Arctic Ocean.

Key words: δ^{13}C, POC, sediment, carbon export flux, western Arctic Ocean

1 Introduction

The Arctic Ocean is especially sensitive to climate change and acts as an important regulator for atmospheric CO_2 concentration (Arrigo et al., 2010; Bates et al., 2006; Boetius et al., 2013). The western Arctic Ocean is a focus of study with respect to CO_2 sequestration mainly due to two reasons. First, the biological pump is running very actively on the broad, shallow continental shelf of the western Arctic Ocean, especially during summer (Chen et al., 2003b; Ma et al., 2005; Moran et al., 2005; Trimble and Baskaran, 2005). Second, the most rapid changes in sea ice cover have occurred in the western Arctic Ocean (Perovich and Richter-Menge, 2009). The resulting changed environmental conditions (stratification, light penetration, nutrient supply, etc.) may greatly influence carbon fixation and the subsequent particulate organic carbon (POC) export from the upper ocean. During summer, the elevated primary production (Lee et al., 2012; Liu, et al., 2011; Liu et al., 2007) would likely decrease surface ocean CO_2 ($[CO_2(aq)]$) dramatically and contribute to higher POC export flux. Although POC export flux in the western Arctic Ocean has been extensively studied, our knowledge of the relationship between POC export flux and surface $[CO_2(aq)]$ is still poor.

Natural stable carbon isotopic composition (δ^{13}C) of marine suspended particulate organic matter (POM) can potentially provide important insights into changes in the environmental conditions under which carbon fixation occurs. With the changed magnitude of CO_2 drawdown, the natural stable carbon isotope signal (δ^{13}C) of marine suspended particulate organic matter will be altered accordingly. Past studies in the Southern Ocean have revealed that the extent of aqueous CO_2 drawdown is a major factor in regulating surface ocean $\delta^{13}C_{POC}$ (Bentaleb et al., 1998; Popp et al., 1999; Zhang et al., 2014). By comparison, the understanding of the controlling factors on $\delta^{13}C_{POC}$ in the western Arctic Ocean is still much more poor to date (Brown et al., 2014; Zhang et al., 2012; and references therein). On the other hand, the δ^{13}C of sedimentary organic carbon has been used for the reconstruction of paleo-pCO$_2$ based on the negative correlation between $\delta^{13}C_{POC}$ and $[CO_2(aq)]$ in surface ocean (Bentaleb et al., 1996; Fischer et al., 1998; Hollander and McKenzie, 1991). These studies were generally conducted in the Southern Ocean, while little is known about the relationship between sedimentary organic δ^{13}C and surface ocean $\delta^{13}C_{POC}$ in the Arctic Ocean.

In this study, we employ natural stable (^{13}C) and radioactive (^{234}Th, ^{238}U) isotope tracers to evaluate the coupling of upper ocean-benthic carbon dynamics in the western Arctic Ocean. One object of this study is to find whether there exist a correlation between POC export flux and the change in $[CO_2(aq)]$ and

thus suspended $\delta^{13}C_{POC}$ in the upper water column of the western Arctic Ocean. The other objective of this study was to couple the $\delta^{13}C$ signals between the suspended POC and the surface sediments, and to validate the use of carbon isotopic composition of surface sediments as a proxy of POC and CO_2 concentration in the upper ocean. It will improve our understanding of the links among climate change, biological production, CO_2, and stable carbon isotope in the Arctic Ocean on a time scale of human concern.

2 Sampling and methods

2.1 *Study area and sampling locations*

Samplings were conducted onboard the icebreaker R/V *Xuelong* during the 2nd Chinese National Arctic Research Expedition (CHINARE) in the western Arctic Ocean (the Chukchi Sea and Canada Basin) from July 30 to September 7, 2003 (Fig. 1). A total of 23 stations were visited, covering a spatial range of 67°–80°N, 146°–172°W. The study area was generally free of ice during the sampling period from US National Snow and Ice Data Center satellite-derived ice distributions (ftp://sidads.colorado.edu/DATASETS/NOAA/G02135/; figure not shown). Note that suspended $\delta^{13}C_{poc}$ was sampled at all stations, CO_2 was measured at 21 stations (except for the stations R13 and B77), ^{234}Th-derived POC export flux was measured at 18 stations, and surface sedimentary organic $\delta^{13}C_{sed}$ was measured at 11 stations.
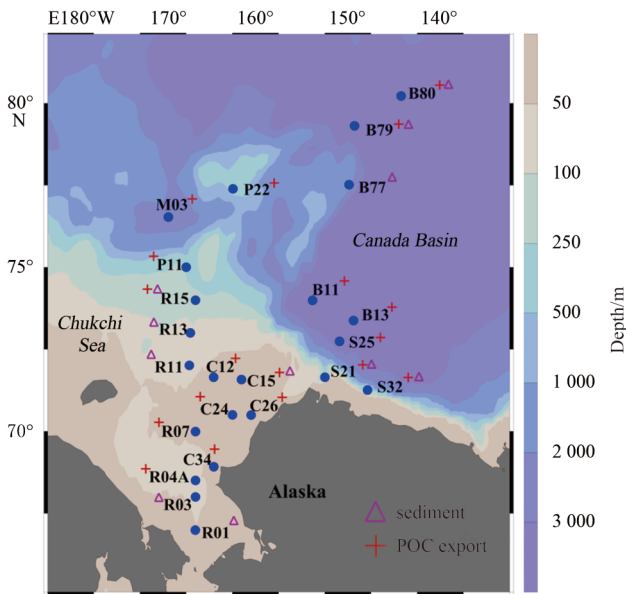

Fig. 1. Sampling stations (closed circles in blue) in the western Arctic Ocean during 2003 CHINARE cruise. Note that suspended $\delta^{13}C_{POC}$ was sampled at all stations, CO_2 was measured at 21 stations (except for Stas R13 and B77), ^{234}Th-derived POC export flux was measured at 18 stations (indicated by superscript crosses in red), and surface sedimentary organic $\delta^{13}C_{sed}$ was measured at 11 stations (indicated by superscript triangles in pink).

2.2 *Environmental parameters (T, S, carbon dioxide)*

Seawater temperature and salinity were recorded using CTD-mounted sensors, and data were provided by the CHINARE project (data source: http://www.chinare.org.cn/pages/metadataDeDisplayBrief.jsp?difId=5587). Concentrations of dissolved

carbon dioxide [CO_2(aq)] in surface (0 m) water were calculated from the partial pressure of CO_2 (pCO$_2$) measured by a shipboard LI-COR 6262 CO_2/H$_2$O infrared gas analyzer using the solubility constants after Weiss (1974). Details are given elsewhere (Chen and Gao, 2007).

2.3 *$\delta^{13}C_{POC}$ in suspended particles*

Samples for $\delta^{13}C_{POC}$ analyses were collected at all stations. Briefly, about 2 L of seawater samples were collected by a CTD rosette system and filtered onto precombusted (400°C, 4 h) Whatman GF/F filters (0.7 μm) for carbon isotope measurements. The filters were rinsed with 0.1 mol/L HCl to eliminate inorganic carbonate and then washed with Milli-Q water. The filters were stored frozen (–20°C) while on the sea. After returning to the land laboratory, the filter samples were dried (60°C) for 24 h and wrapped into tin capsules for simultaneous measurements of POC concentration and its ^{13}C abundance on a Finnigan MAT Delta^{plus} XP mass spectrometer interfaced with an elemental analyzer (Carlo Erba NC2 500). The stable carbon isotopic composition (versus VPDB) is expressed in the conventional δ notation (given in ‰):

$$\delta^{13}C = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1\right) \times 1\,000, \tag{1}$$

where R is the ^{13}C/^{12}C ratio. The reproducibility of δ^{13}C measurements was better than ±0.2‰.

2.4 *POC export flux*

POC export fluxes were estimated from ^{234}Th/^{238}U disequilibrium (half life: $t_{1/2}$=24.1 d and $t_{1/2}$=4.5×10^9 a for ^{234}Th and its parent nuclide ^{238}U, respectively) at 18 stations (Fig. 1). Seawater samples were collected using a submersible pump at identical depth intervals (shelf stations: 0, 10, 20, 30, 40 m; slope and basin stations: 0, 25, 50, 75, 100 m) covering the upper water column above the export depth. Water samples were then mixed to 30 L at a certain volume ratio (surface/bottom layer: 3.75 L; other layers: 7.5 L for measuring total ^{234}Th activity (A_{Th}). By applying such sampling strategy, we will obtain the average ^{234}Th activity above the export depth. For measurements of particulate ^{234}Th activity (A_{pTh}) at the export depth (40 m or 100 m), 22 L seawater was collected and filtered through a mixed cellulose ester membrane (0.45 μm). Filters were rinsed with Milli-Q water and then stored frozen. The protocols for chemical separation and purification for ^{234}Th analysis were conducted in the land laboratory as soon as possible (Ma et al., 2005). The ^{234}Th activity (Bq/m^3) was immediately counted on a low-level beta counter (BH1216, Beijing Nuclear Instrument Factory) (Chen et al., 1997). Alpha counting was conducted again with silicon surface barrier detectors (Octete^{TM} plus, EG&G) to determine the yield of the added ^{228}Th activity. The ^{234}Th activity was decay-corrected to the sampling time. The ^{238}U activity (A_U, Bq/m^3) was calculated from salinity (S) using an empirical equation (A_U=1.31S–5.25; Owens et al., 2011), which is somewhat refined relative to the previously widely accepted one (A_U=1.180 2 S; Chen et al., 1986). It has been corroborated that the newly refined equation is derived from a much larger data set and should provide more precise estimates of ^{238}U activity from seawater salinity (Owens et al., 2011).

POC export flux was estimated using an irreversible scavenging model (Buesseler et al., 1992). POC export flux (F_{POC}, mmol/(m^2·d), calculated by carbon) can be calculated using the integrated ^{234}Th removal flux (F_{Th}, Bq/(m^2·d)) and the ratio of POC concentration (c(POC)) to particulate ^{234}Th activity (A_{pTh}) at the export depth:

$$F_{POC} = F_{Th} \times \frac{c(POC)}{A_{pTh}}. \tag{2}$$

In order to eliminate the effect of different integrated depths for shelf and slope/basin stations, the depth-averaged POC export fluxes (E_{POC}, mmol/(m³·d), calculated by carbon) in the upper water column were derived (Chen et al., 2003b):

$$E_{POC} = \frac{F_{POC}}{z},\qquad(3)$$

where z (m) represents the export depth. E_{POC} represents the averaged POC export flux from the upper water column, which is essential for comparing the efficiency of biological pump in the shelf and the basin. The residence time of total ^{234}Th (τ, d) can be calculated as follow (Chen et al., 2003b):

$$\tau = \frac{A_{Th}}{\lambda \times (A_U - A_{Th})},\qquad(4)$$

where λ is the decay constant (0.028 76 d^{-1}) of ^{234}Th.

2.5 Sedimentary organic $\delta^{13}C_{sed}$

Surface sediments were collected at 11 stations (Fig. 1) for the determination of δ^{13}C of organic matter ($\delta^{13}C_{sed}$). Detailed information of sampling, sample treatment and measurement were provided by the CHINARE program and can be found elsewhere (Chen et al., 2006).

3 Results

3.1 Temperature, salinity and [CO₂(aq)]

Sea surface temperature (–1.55–7.94°C) were much higher on the shelf in south of 72°N, while it varied little (at about –1.5°C) north of 72°N (Figs 2a and e). Sea surface salinity ranged between 27.44 and 32.57, and the higher values were encountered on the shelf (Figs 2b and f). pCO₂ (155–391 μatm, average of 258 μatm)

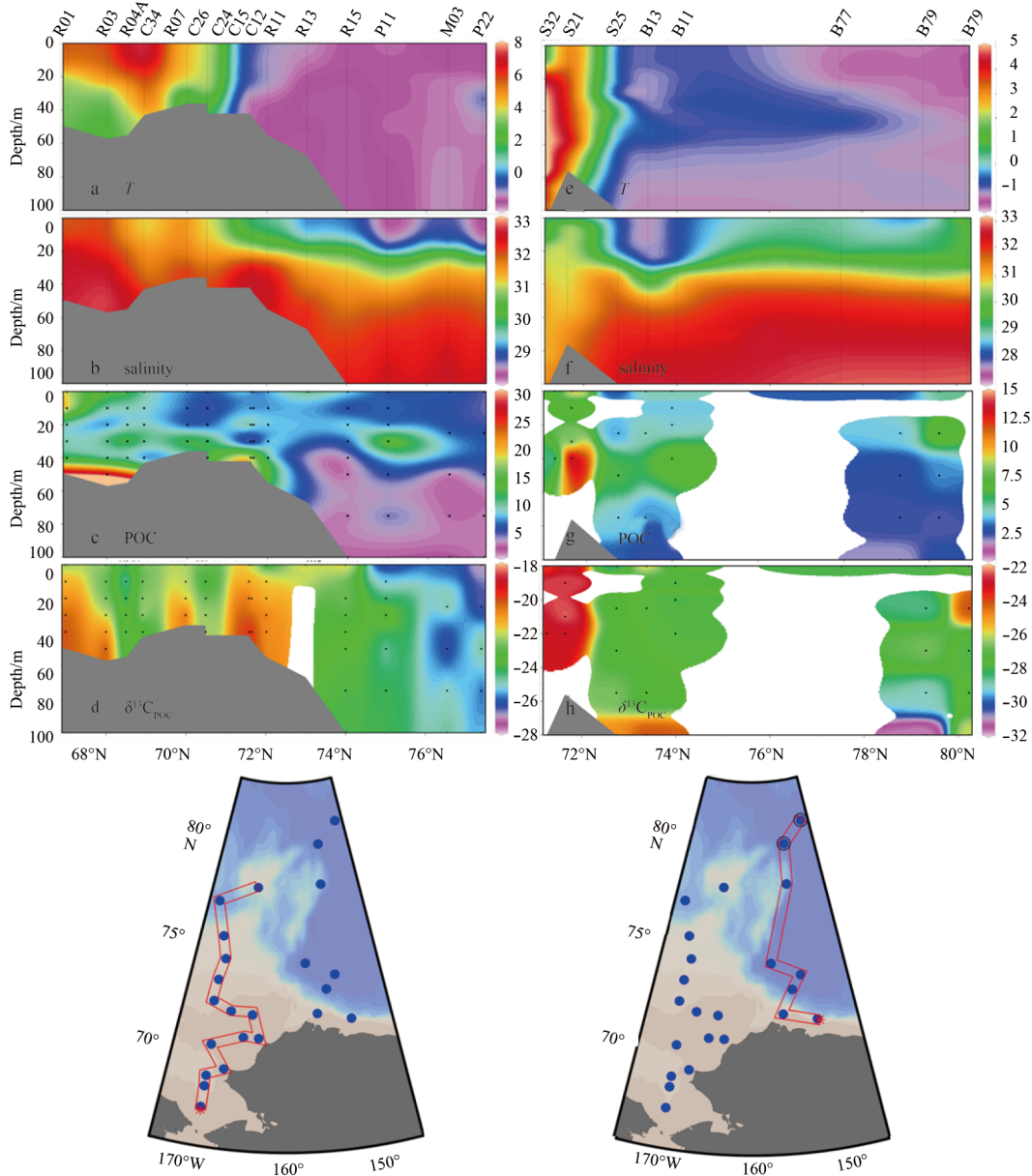**Fig. 2.** Depth profiles of temperature, salinity, suspended POC concentration and $\delta^{13}C_{POC}$ in the upper water column along about 170°W (a, b, c and d) and 155°W (e, f, g and h). The transect pathways are shown in the bottom. a and e. Temperature (°C), b and f. salinity, c and g. POC concentration (μmol/L), and d and h. $\delta^{13}C_{POC}$ (‰).

was generally below the equilibrium values with atmosphere. Sea surface $[CO_2(aq)]$ ranged between 9.7 and 27.6 μmol/L, with a mean value of 16.6 μmol/L. The distribution pattern of satellite remote sensing chlorophyll concentration (Fig. 3) was generally anti-correlated with that of surface $[CO_2(aq)]$ (Fig. 4a). There is an obvious increase in $[CO_2(aq)]$ in the deep basin compared with the continental shelf and slope.

3.2 *POC and $\delta^{13}C_{POC}$*

POC concentrations ranged from 1.5 μmol/L to 28.3 μmol/L in the upper water column (<100 m), and much higher values were observed in the shelf area (Figs 2c and g). Surface $\delta^{13}C_{POC}$ ranged widely from –28.50‰ to –21.14‰ and consistently much higher values were observed on the shelf and slope compared to the deep basin (Figs 2d and h). Our $\delta^{13}C_{POC}$ values generally fall in reported value ranges in other high-latitude sea areas, such as the southeastern Bering Sea and the Southern Ocean (Bentaleb et al., 1998; Guo et al., 2004; Popp et al., 1999).
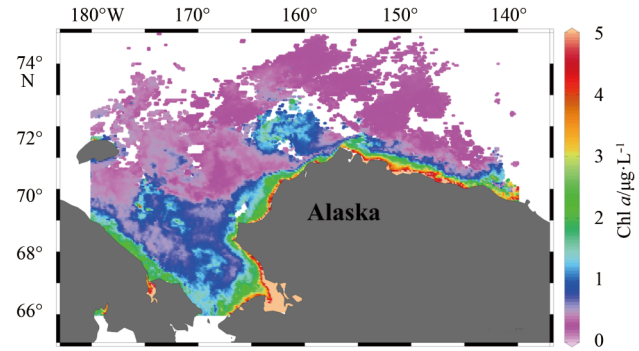

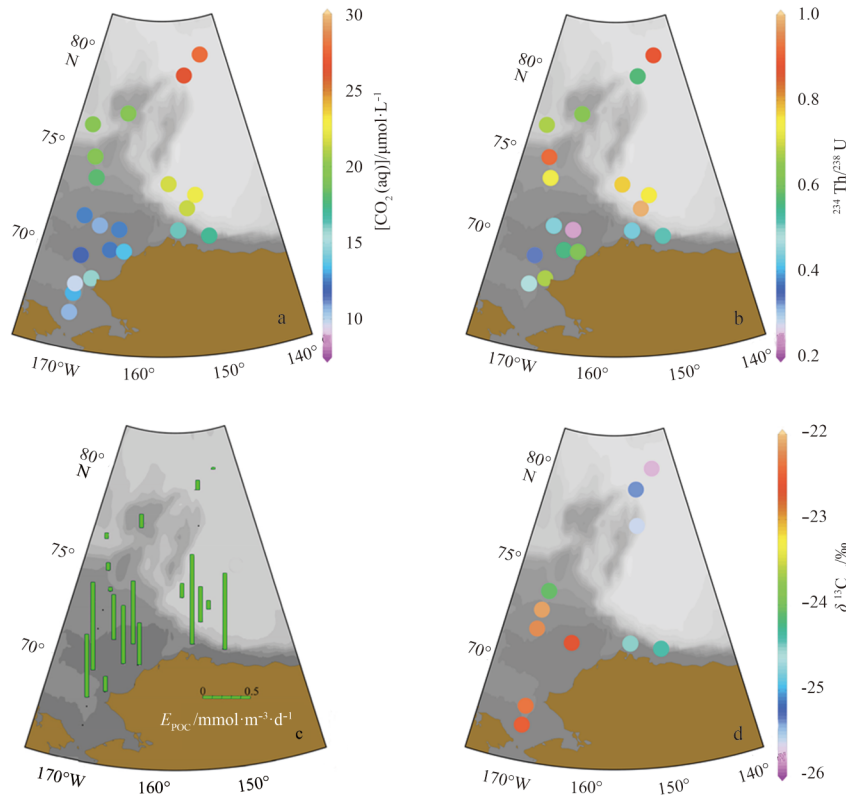**Fig. 3.** Monthly mean chlorophyll from MODIS satellite remote sensing (August 2003) (source:http://oceanwatch. pifsc.noaa.gov/las/).

Fig. 4. Distributions $[CO_2(aq)]$ at surface water (a), the averaged $^{234}Th/^{238}U$ activity ratio in the upper water column (b), the depth-averaged POC export flux from the upper water column (c), and surface sedimentary organic $\delta^{13}C$ (d). Note that the upper water column was chosen as the upper 40 m in the shelf, and 100 m in the slope/basin.

3.3 *$^{234}Th/^{238}U$ disequilibria and E_{POC}*

Disequilibria between ^{234}Th and its parent radionuclide ^{238}U were commonly observed (except for the slope station S25) in the upper water column, with ratios of total ^{234}Th to ^{238}U activities (A_{Th}/A_U) ranging from 0.23 to 1.02 (average 0.62±0.21) (Fig. 4b). Relatively low $^{234}Th/^{238}U$ values (0.23–0.73, average 0.50, n=9) were observed on the shelf. The depth-averaged POC export fluxes (E_{POC}) in the upper water column ranged from 0.02 to 0.94 mmol/(m³·d), and higher values were occurred on the shelf (Fig. 4c). The residence times of total ^{234}Th (τ) ranged from 10.6 d at Sta. C15 to 340.0 d at Sta. P11 (Table 1). The residence time of

total ^{234}Th at the continental shelf stations was much shorter than those at the slope and basin stations ((42.0±27.6) d vs (115.9±109.9) d).

3.4 *$\delta^{13}C_{sed}$*

$\delta^{13}C_{sed}$ in sedimentary organic matter varied from –25.80‰ to –22.16‰, being in agreement with previously reported results around this region (Naidu et al., 1993; Ruttenberg and Goñi, 1997). Higher values were generally observed on the shallow shelf (Fig. 4d), which is similar to the spatial pattern of surface ocean $\delta^{13}C_{POC}$.

4 Discussion

4.1 *POC export flux versus [CO₂(aq)] and δ¹³C_POC*

Previous studies have shown that suspended POC in the western Arctic Ocean surface waters during summer mainly derive from phytoplankton production rather than from terrestrial organic matter contribution (Brown et al., 2014; Liu et al., 2007; Zhang et al., 2012). Meanwhile, recent studies have shown that $\delta^{13}C_{POC}$ values are negatively correlated to $[CO_2(aq)]$ in surface waters in the western Arctic Ocean during summer (Brown et al., 2014; Zhang et al., 2012). Although the distribution of $[CO_2(aq)]$ is a combining result of both solubility and biological activities, the variations in solubility solely may not be responsible for the observed large variability of $[CO_2(aq)]$ as observed in the western Arctic Ocean during summer, while the biological pump (POC export) played a decisive role (Chen and Gao, 2007). Phytoplankton bloom was evident on the shelf from chlorophyll distribution of this cruise (Fig. 3) or directly measured results of previous CHINARE cruises (Lee et al., 2012; Liu et al., 2011; Liu et al., 2007). By comparison, the slope and basin are characterized by much lower chlorophyll concentrations. We propose that with elevated primary production, an enhanced CO_2 drawdown and meanwhile an increase in POC export from the upper water column should be resulted in. This hypothesis is confirmed by a negative correlation between dissolved CO_2 concentration in surface water and POC export flux (Fig. 5). In other words, the occurrence of the most enriched $\delta^{13}C_{POC}$ in the western Arctic Ocean
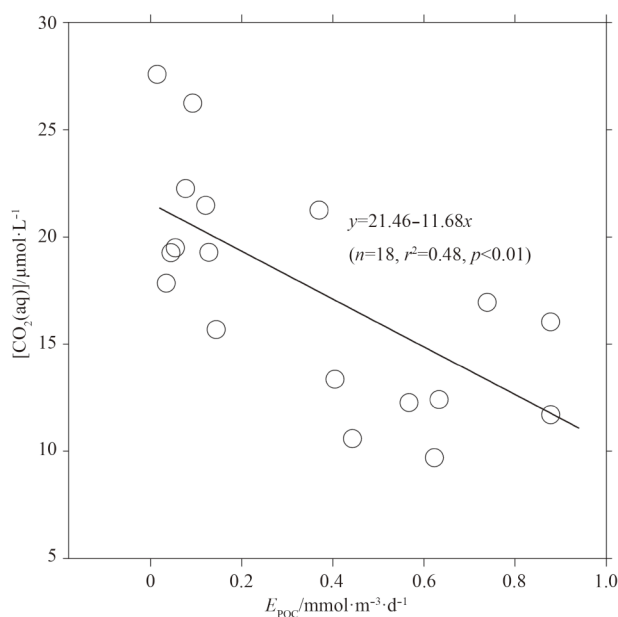

Fig. 5. Relationship between surface seawater CO_2 concentration ($[CO_2(aq)]$) and the depth-averaged POC export flux (E_{POC}) in the upper100 m.

appears to be related to the greatest amount of POC export flux from the upper ocean. It has been well accepted that there may exist a correlation between POC export flux and surface ocean CO_2 concentration based on the results from North Pacific Subtropical Gyre (Emerson et al., 1997). However, direct evidence from field studies are lacking since then (Rutgers van der Loeff et al., 2011). Our finding is similar to that observed in the Southern Ocean, where reduced surface seawater pCO₂ values were correl-

ated to the low ²³⁴Th activities but high chlorophyll concentrations in the Polar Front Zone (Rutgers van der Loeff et al., 2011). We suggest that further studies are undoubtedly necessary to better reveal the correlation between POC export flux and surface ocean CO_2, as such correlation may have large spatial and temporal variability and be subject to changes in the polar oceans with highly variable environmental conditions, such as sea ice (advance, retreat, melting, etc.).

Previous studies have confirmed that biological pump runs actively in the western Arctic Ocean during summer (Chen and Gao, 2007; Chen et al., 2003a; Chen et al., 2003b; Ma et al., 2005; Moran et al., 2005). This is especially the case for the wide shallow Chukchi shelf, where elevated primary production is evident during past CHINARE cruises in summer (Lee et al., 2012; Liu et al., 2011; Liu et al., 2007; Yang et al., 2006). The magnitude of carbon isotopic fractionation during carbon fixation may decrease when aqueous CO_2 concentration is lowered down due to active biological utilization (Francois et al., 1993; Hofmann et al., 2000; Rau et al., 1997). It is quite probable that the subsequent carbon export from the surface ocean may be linked to the variations of $\delta^{13}C_{POC}$ in the surface ocean. Indeed, the ²³⁴Th/²³⁸U activity ratios were negatively correlated to $\delta^{13}C_{POC}$ values (after being weighted by POC concentration) in the upper water column (Fig. 6), thus corroborating the idea that biological pump is coupled with surface $[CO_2(aq)]$ and $\delta^{13}C_{POC}$.
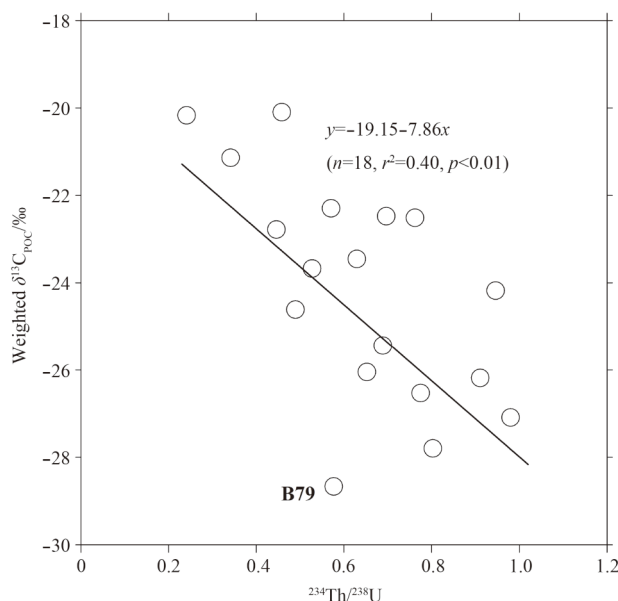
Fig. 6. Relationship between the weighted $\delta^{13}C_{POC}$ and ²³⁴Th/²³⁸U in the upper water column.

4.2 *Coupling of upper ocean and sedimentary carbon isotopic signatures*

A positive correlation between the $\delta^{13}C$ values of surface sediments and the weighted $\delta^{13}C_{POC}$ in the upper water column ($\delta^{13}C_{sed} = 13.64 + 1.56 \times \delta^{13}C_{POC}$, $r^2 = 0.73$, $p < 0.01$; Fig. 7) implies that sediments may have recorded the isotopic patterns of the POC from the upper water column over much of the western Arctic Ocean. This idea is further supported by the rapid export of POC from the upper ocean as evidenced by the short residence times of ²³⁴Th in this area (Table 1). The relatively low residence times of total ²³⁴Th (Table 1) in the upper water column indicates active scavenging and removal by particles. Although the residence

Table 1. Sampling information and parameters at surface seawater (T, S, pCO$_2$, [CO$_2$(aq)], POC, δ^{13}C$_{POC}$), in the upper water column (average E_{POC}, A_{Th}/A_U, τ) and for the surface sediment (δ^{13}C$_{sed}$)

Station	Depth/m	West longitude/(°)	North latitude/(°)	Sea surface (0 m)						Upper water column			
				T/°C	S	pCO$_2$/ µatm	[CO$_2$(aq)]/ µmol·L^{-1}	POC/ µmol·L^{-1}	δ^{13}C$_{POC}$/‰ vs VPDB	Export depth/m	E_{POC}/ mmol·m^{-3}·d^{-1}	A_{Th}/ A_U	τ/d	δ^{13}C$_{sed}$/‰ vs VPDB
R01	50	169.01	66.99	5.72	31.95	198	10.5	17.6	−22.5		nd	nd	nd	−22.5
R03	55	169.00	68.00	3.34	32.57	227	13.1	11.9	−22.3		nd	nd	nd	−22.4
R07	35	169.00	70.00	4.62	31.99	212	11.7	6.8	−22.1	30	0.88	0.34	17.2	nd
R11	50	169.67	72.01	−1.17	29.68	178	12.4	7.6	−24.2		nd	nd	nd	−22.3
R13	67	169.55	73.00	−0.91	29.22	nd	nd	10.0	−22.0		nd	nd	nd	−22.2
R15	175	168.99	74.00	−1.47	29.49	253	17.8	8.0	−21.8	40	0.03	0.76	95.8	−24.1
C12	45	167.03	71.65	−0.65	29.49	155	10.6	1.8	−22.6	40	0.44	0.46	27.7	nd
C15	42	164.01	71.58	−0.87	30.45	181	12.4	11.5	−21.1	40	0.63	0.24	10.6	−22.7
S21	76	154.98	71.65	2.94	27.44	267	16.0	9.3	−22.7	40	0.88	0.45	26.1	−24.5
C24	42	164.99	70.50	3.20	31.13	210	12.3	5.6	−22.3	40	0.57	0.57	42.9	nd
C26	36	162.98	70.49	4.96	31.20	244	13.4	5.4	−23.3	30	0.40	0.63	54.3	nd
C34	43	167.01	68.92	7.94	30.93	318	15.7	8.9	−22.4	40	0.14	0.70	71.9	nd
R04A	52	169.00	68.50	7.63	31.49	195	9.7	13.1	−24.4	40	0.62	0.49	31.4	nd
P11	263	169.99	75.01	−1.27	28.58	274	19.3	5.5	−26.9	40	0.04	0.95	340.0	nd
B11	3 000	156.33	74.00	−0.98	27.98	308	21.5	4.5	−27.9	40	0.12	0.80	114.0	nd
S32	2 300	150.38	71.26	1.52	29.37	270	16.9	5.9	−24.0	40	0.74	0.53	35.9	−24.4
M03	2 300	171.93	76.54	−1.55	29.16	275	19.5	5.6	−26.0	100	0.05	0.69	69.8	nd
B13	3 800	151.88	73.38	−1.02	27.56	318	22.3	4.5	−25.6	100	0.08	0.77	102.0	nd
S25	3 000	153.40	72.74	−0.65	28.15	309	21.2	2.7	−28.5	100	0.37	0.98	20.2	nd
B77	3 000	152.37	77.52	−1.42	28.88	nd	nd	5.4	−27.0		nd	nd	nd	−25.6
B80	3 750	146.74	80.22	−1.52	29.86	391	27.6	4.9	−27.1	100	0.01	0.91	258.0	−25.8
B79	3 800	151.79	79.31	−1.47	28.47	370	26.2	2.9	−28.1	100	0.09	0.58	43.8	−25.4
P22	326	164.93	77.40	−1.49	28.68	272	19.3	4.1	−27.0	100	0.13	0.65	59.6	nd

Note: nd represents no data. 1 atm=101 325 Pa.

time of particulate ^{234}Th was not measured in this study, it should be much shorter than that of total ^{234}Th. It has been revealed that in the Beaufort Sea the residence time of particulate ^{234}Th was around 12–18 d in the upper water column (Moran and Smith, 2000). In the western Arctic Ocean, most particulate organic carbon was rapidly sinking to benthos with a mean particle settling rate of about 60 m/d (Ashjian et al., 2005). Moreover, profiles of polyunsaturated fatty acids (PUFAs) and several algal sterols revealed the dominance of biogenic carbon on the broad, shallow Chukchi shelf and slope, and suggested that episodic pulses of marine material may be incorporated relatively unaltered into sediments (Belicka et al., 2004). The rapid scavenging and removal of particles would likely minimize the alterations of carbon isotopic signature by remineralization during particle's sinking to the seafloor. Since the surface POC δ^{13}C is dependent on the concentration of dissolved CO$_2$ in the western Arctic Ocean (Brown et al., 2014; Zhang et al., 2012), such a surface ocean-benthic correlation observed here implies that δ^{13}C ratios in the sedimentary organic matter has the potential to be a record for changes in δ^{13}C$_{POC}$ and [CO$_2$(aq)] in the upper Arctic Ocean.

The deviation of δ^{13}C (±3.0‰) between surface sediments and suspended POC should be a result of complex factors, including the heterotrophic recycling and remineralization within the upper water column, i.e., preferential use of ^{12}C over ^{13}C during bacterial utilization (Lapoussière et al., 2011) and the perturbations by post-sedimentary processes (such as degradation of organic matter by early diagenesis, contribution from lateral transport, etc.) (Boetius et al., 2013; Brown et al., 2014; Guo et al., 2004; Lehmann et al., 2002). Relatively large deviation was seen at the deep basin stations. Since the basin stations are less pro-
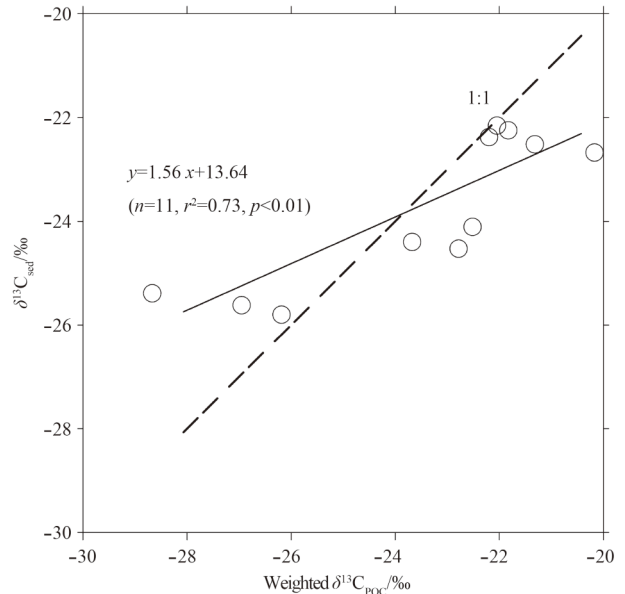

Fig. 7. Relationship of weighted δ^{13}C$_{POC}$ in the upper water column and surface sedimentary organic δ^{13}C$_{sed}$. The dashed line represents the 1:1 mixing line.

ductive than shallow waters, significant degradation may have occurred before the organic matter reaches the sediment-water interface (Belicka et al., 2002). Increased degradation and the variability of the fraction of marine organic carbon may be the

causes. Besides, it is worth noting that sedimentary $\delta^{13}C$ signatures are best explained by the averaging of organic carbon deposition over time, whereas water column samples represent bloom-related processes that change throughout the seasons, which may also have led to the observed discrepancy of $\delta^{13}C_{POC}$ versus $\delta^{13}C_{sed}$ (Villinski et al., 2000). Similarly, studies also found that there exists a discrepancy of about 3.0‰ for $\delta^{13}C$ values of suspended POM ((–24.5±0.9)‰) and sedimentary organic matter ((–21.5±1.2)‰) in the southeastern Bering Sea (Guo et al., 2004; Smith et al., 2002). We suggest that more studies are needed for better understanding the coupling of upper ocean-benthic carbon dynamics in the Arctic Ocean in the future.

5 Conclusions

In this study, we evaluated the coupling of upper ocean-benthic carbon dynamics in the ice-free western Arctic Ocean using natural stable and radioactive isotope tracers. ^{234}Th-based POC export flux was negatively correlated to surface seawater dissolved CO_2 concentration ($[CO_2(aq)]$), implying that the strengthened biological pump on the shelf have significantly lowered $[CO_2(aq)]$ and altered the magnitude of isotopic fractionation during carbon fixation. Values of $\delta^{13}C$ of surface sediments ($\delta^{13}C_{sed}$) are positively correlated to those of $\delta^{13}C_{POC}$ in the upper ocean, suggesting that the POC isotopic signals from the upper ocean have been recorded in the sediments. It implies that there probably exists an upper ocean-benthic coupling of carbon dynamics in the western Arctic Ocean, possibly making the sedimentary $\delta^{13}C$ record an indicator of paleo-CO_2.

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