Variations in the isotopic composition of particulate organic carbon and their relation with carbon dynamics in the western Arctic Ocean

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A B S T R A C T
The relation between the dissolved carbon dioxide (CO₂) and the stable isotopic composition of particulate organic matter in the water column has not been well quantified, but this information could help provide a better understanding of carbon dynamics in a warmer Arctic Ocean. The stable carbon isotopic composition of suspended particulate organic carbon (δ¹³CPOC) in the surface waters of the western Arctic Ocean was measured during July–September 2003, to evaluate the spatial variability of δ¹³CPOC and its key controlling factors. Values of δ¹³CPOC fell within the range of −28.5‰ to −21.1‰, with an average of −24.5 ± 2.3‰. The spatial variability of δ¹³CPOC showed a general decreasing trend from shallow waters in the continental shelf toward the deeper, colder waters in the basin. A negative correlation between δ¹³CPOC and the dissolved CO₂ concentration in surface waters was observed, indicating that carbon isotopic fractionation during photosynthesis was largely dependent on the dissolved CO₂ concentration. Compared to the solubility pump, biological processes may play a more important role in determining the distribution and variation of δ¹³CPOC in the western Arctic Ocean during summer. The coupled relationship between CO₂ concentration and stable isotopic composition of particulate organic matter has the potential to be used for reconstruction of sea-surface CO₂ changes in the past, provided a quantitative relationship of δ¹³C between POC and sediments can be established.

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1. Introduction
The natural stable carbon isotopic composition (δ¹³CPOC) of marine suspended particulate organic matter (POM) can potentially provide important insights into changes in the environmental conditions under which carbon fixation occurs. An understanding of the spatial variability and the key controlling factors of δ¹³CPOC is therefore indispensable for the use of δ¹³CPOC as a proxy in studies of the marine carbon cycle and environmental changes (Fischer, 1991; Hofmann et al., 2000; Laws et al., 1995; Popp et al., 1999; Rau et al., 1997).

Planktonic δ¹³CPOC is a function of the δ¹³C of the inorganic carbon source for organic matter production and the isotopic fractionation factor during photosynthesis. During photosynthesis, the isotopic fractionation plays a decisive role (Keller and Morel, 1999; Laws et al., 1995). A negative correlation between δ¹³CPOC and dissolved carbon dioxide concentration [CO₂(aq)] has been observed in many previous studies, revealing that [CO₂(aq)] is a major factor in controlling the δ¹³C composition of POC (Francois et al., 1993; Hofmann et al., 2000; Kennedy and Robertson, 1995; Rau et al., 1997, 1992).

The Arctic Ocean is especially sensitive to climate change and may act as an important sink or source for atmospheric CO₂ (Bates et al., 2006; Cai et al., 2010; Dickson, 1999; Kaltin and Anderson, 2005; Murata and Takizawa, 2003; Walsh, 1989). Applications using stable isotopic composition should improve our understanding of carbon dynamics and its response to climate and environmental changes in the Arctic Ocean. Previous studies have shown that the biological pump in the western Arctic Ocean is actively running in summer (Chen et al., 2002, 2003; Ma et al., 2005; Moran et al., 2005; Trimble and Baskaran, 2005). The active biological uptake of CO₂ in the surface ocean decreases [CO₂(aq)], and at the same time contributes to the POC export flux (namely, export production). Unfortunately, measurements of the stable isotopic composition of particulate organic matter in the Arctic Ocean remain scarce. There are very few available or published data allowing examination of the relationship between δ¹³CPOC and [CO₂(aq)] in the Arctic Ocean. Thus, measurements of stable isotopic composition are sorely needed, because the dependence of δ¹³CPOC on [CO₂(aq)] observed in other marine environments...
may not be applicable in the Arctic Ocean, and carbon isotopic fractionation may also be controlled by other factors such as growth rate, phytoplankton species composition, trophic effects, and water temperature (e.g., Cullen et al., 2001; Goericke and Fry, 1994; Guo et al., 2004; Hofmann et al., 2000; Tamelander et al., 2006).

The release of anthropogenic CO₂ (mainly derived from fossil fuel burning and deforestation) has been increasing, especially in recent decades, and a large fraction of these emissions has been taken up by the ocean (Gruber, 1998; Sabine et al., 2004; Siegenthaler and Sarmiento, 1993). As an isotopically “light” source, anthropogenic CO₂ invading the upper ocean will result in an increase in surface [CO₂(aq)] but a decrease in δ¹³CO₂(aq) (known as the Suess effect). Therefore, a subsequent decrease of δ¹³CPOC in the water column can be predicted (Bauch et al., 2000; Druffel and Benavides, 1986; Quay et al., 2003, 1992; Schell, 2001). In the Arctic Ocean, a decrease of about 2‰ in phytoplankton δ¹³C since the Industrial Revolution has been attributed to the input of anthropogenic CO₂ (Bauch et al., 2000).

In the present study, samples collected from the western Arctic Ocean were measured for stable carbon isotopic composition (δ¹³C) and other parameters to investigate spatial variability in the δ¹³C values of suspended POM, the role of CO₂(aq) in controlling the δ¹³CPOC, and the effects of the solubility and biological pumps on δ¹³CPOC. The relationship between surface [CO₂(aq)] and δ¹³CPOC was further used to assess the possible impact of anthropogenic CO₂ on the δ¹³CPOC of the western Arctic Ocean.

2. Materials and methods

2.1. Study area and sampling locations

Water and suspended particulate samples were collected onboard the icebreaker R/V XUELONG from July to September 2003 during the Second Chinese Arctic Research Expedition (CHINARE). A total of 31 stations were sampled for POC, PON, and δ¹³CPOC measurements in the western Arctic Ocean, including the northern Bering Sea (3 stations near the Bering Strait), the eastern Chukchi Sea, the western Beaufort Sea, and part of the Canada Basin (Fig. 1). Seawater samples were collected using a CTD rosette system. Temperature, salinity, and Chl-a concentration data were provided by the CHINARE program (www.polar.gov.cn).

2.2. Sampling and measurements of POC, PON, and δ¹³CPOC

For POM and δ¹³CPOC measurements, about 2 l of surface (~1 m) seawater samples were filtered onboard ship through a precombusted (400 °C, 4 h) Whatman GF/F membrane. After filtration, the filters with suspended POM samples were rinsed with 10 ml 0.1 mol/dm³ HCl and 30 ml Milli-Q water to remove inorganic carbonate, and then stored frozen. While in the laboratory, the filter samples were dried at 60 °C and wrapped into tin capsules for measurements of POC, PON, and δ¹³CPOC.

Concentrations of POC, PON, and stable carbon isotopic composition (in term of δ¹³C) were measured on a Finnigan MAT Delta plus XP mass spectrometer interfaced with an elemental analyzer (Carlo Erba NC2500). The δ¹³C value (versus PDB) of POM sample was defined as the following:

\[
\delta^{13}C_{POC} = \left( \frac{R_{sample}}{R_{standard}} - 1 \right) \times 1000
\]

The reproducibility of δ¹³C measurements was within ± 0.2‰.

2.3. Measurements of pCO₂ and [CO₂(aq)]

The partial pressures of CO₂ (pCO₂, µatm) in the surface waters were measured using a shipboard LI-COR 6262 CO₂/H₂O infrared gas analyzer. Standard carbon dioxide gas mixtures from the National Research Center of Standard Materials of China were used for calibration, with concentrations of 285, 348, and 401 ppmv [CO₂/air]. The system accuracy was ± 1.5 µatm (Chen and Gao, 2007).

Concentrations of dissolved CO₂ ([CO₂(aq)]) were calculated from pCO₂, temperature (T), and salinity (S), using the solubility constants (K₀) established by Weiss (1974):

\[
[KO₂(aq)] = K₀ pCO₂
\]

\[
\ln K₀ = a₁ + a₂ \frac{T}{100} + a₃ \ln \left( \frac{T}{100} \right) + S \left[ b₁ + b₂ \frac{T}{100} + b₃ \left( \frac{T}{100} \right)^2 \right]
\]

3. Results

3.1. Hydrographic features

The spatial distributions of surface water temperature and salinity are shown in Fig. 2A and B. Surface water temperature ranged from −1.55 to 10.50 °C, with an average of 1.95 °C in the study area (Table 1). Temperature decreased northward from an average of ~9 °C in the northern Bering Sea to ~3 °C at stations shallower than 50 m on the Chukchi Shelf, and fell to below zero (about −1 °C) at deeper stations in the Canada Basin. Water temperature can alter the solubility of CO₂, although primary production and organic matter degradation also play an important role.

Surface water salinity ranged from 27.44 to 32.57, with an average of 29.76 (Table 1). Except for several extremely low-salinity values (~28) that were observed in the deep basin, likely caused by sea-ice melt, salinity (~31) did not vary dramatically over the northern Bering Sea and the Chukchi Shelf. Generally, low surface-water salinity and its spatial distribution could be attributed to the significant dilution effect of sea ice melting in summer.

3.2. Distribution of POC, PON, and C/N ratios

The spatial distributions of POC and PON are depicted in Fig. 2C and D. POC concentrations in the surface water varied between 1.8
and 19.1 μM, with an average value of 7.7 ± 4.0 μM, while PON concentrations varied between 0.3 and 3.5 μM, with an average value of 1.2 ± 0.7 μM (Table 1). The average C/N ratio (6.7 ± 1.4) deviated little from the Redfield ratio of 6.6 (106:16), with a range between 5.1 and 11.9. These POC and PON concentrations and C/N ratios are similar to those reported in previous studies (Chen et al., 2003; Ma et al., 2005; Trimble and Baskaran, 2005). POC and PON concentrations generally decreased with increase in latitude, showing similar distribution patterns as surface water temperature and salinity (Fig. 2A and B). The observed POC/PON ratios in the western Arctic Ocean are considerably lower than those measured for terrestrial POM (27 ± 8) derived from the Yukon and Mackenzie Rivers (Guo et al., 2011; Unpublished Data). The positive correlation between POC and temperature, together with the average C/N ratio of POM close to the Redfield ratio, suggested that particulate organic matter collected during the sampling period was mainly from marine-derived organic matter.

3.3. Distribution of δ13CPOC

The δ13CPOC fell in a wide range between −28.5‰ and −21.1‰, with an average value of −24.5 ± 2.29‰ (Table 1).
The north Bering Sea–Chukchi Shelf area had a higher average δ13CPOC value of −22.9‰ (n=17, ranging from −24.6‰ to −21.1‰). The average δ13CPOC value decreased dramatically to about −26.5‰ (from −28.5‰ to −22.7‰, n=14) at deep-water stations (Fig. 2E). To the best of our knowledge, such great variations in δ13CPOC resemble those observed for temperature and POC. In addition to changes in δ13CPOC along the latitudinal gradient, with higher values near the Bering Strait and Chukchi Shelf and lower values toward the deep basin, a west to east increasing trend from the Chukchi Shelf to the Beaufort Sea was also evident (Fig. 2E).

The values of surface water δ13CPOC measured in our study area compared well with those reported previously for other marine environments. They are close to those observed in the southeastern Bering Sea in summer (from −27.1‰ to −23.4‰ with an average of −24.5‰, Guo et al., 2004), but lighter than those found in low latitude sea areas, such as in the subtropical southwestern Indian Ocean (from −28.4‰ to −16.5‰ with an average of −23.7‰, Francois et al., 1993) or the equatorial Pacific Ocean (from −21.5‰ to −20.8‰ with an average of −21.1‰, Laws et al., 1995). However, our δ13C values are higher than those encountered in the Southern Ocean (from −29.7‰ to −21.9‰ with an average of −26.6‰, Dehairs et al., 1997; Kennedy and Robertson, 1995). This is consistent with the reported latitudinal increasing trend of surface ocean δ13CPOC toward the tropics in both hemispheres (Goericke and Fry, 1994; Hofmann et al., 2000).

The particulate organic matter during the sampling period was derived predominantly from marine organic matter, and terrestrial organic matter did not seem to have a noticeable impact on δ13CPOC variations in the study area. Three lines of evidence support this statement. First, the average C/N ratio of POM was 6.7 ± 1.4 (Table 1) and similar to the Redfield ratio. Second, a significant positive correlation between POC and the Chl-a

**Table 1**

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<th>Latitude (N)</th>
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<th>S</th>
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<th>POC (µM)</th>
<th>PON (µM)</th>
<th>C/N (molar)</th>
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Note: nd represents no data.
concentration was observed (Fig. 3), also indicating a marine origin of the POM. A higher Chl-a concentration or higher biomass could result in a higher POC concentration. Third, $\delta^{13}$C$_{POC}$ decreased from the shelf to the deep basin (Fig. 2E), ruling out the possibility of a major contribution of terrestrial organic matter in the study area. The $\delta^{13}$C$_{POC}$ value of the terrestrial end member for the northern Bering–Chukchi–Beaufort Sea was reported as $-27\%$$_{o}$, based on the data from major Arctic rivers, such as the Colville River, Mackenzie River, Lena River, and Yukon River (Guo and Macdonald, 2006; Minagawa et al., 1991; Naidu et al., 2000, 1993; Ruttenberg and Goni, 1997; Schell, 1983). Although the $\delta^{13}$C of marine-derived POC in the study area has not yet been reported, it is speculated to be at least 2–3%$_{o}$ heavier than that of terrestrial organic matter (Guo and Macdonald, 2006; Naidu et al., 2000) due to the difference in plant photosynthetic environments. If the influence of terrestrial organic matter is significant in the study area, the $\delta^{13}$C$_{POC}$ values would have increased from the shelf to the deep basin because the inner shelf waters should have received more freshwater and terrestrial organic matter. However, the opposite was true. Thus, POM collected during our sampling period should be predominantly derived from in situ biological production.

4.2. Dependence of $\delta^{13}$C$_{POC}$ on $[\text{CO}_2(\text{aq})]$ 

The $\delta^{13}$C$_{POC}$ signatures of biogenic POM should be controlled by biological fractionation during synthesis of organic material. Our results show that the surface water $\delta^{13}$C$_{POC}$ decreased northward and had the mirror pattern with dissolved carbon dioxide (Fig. 2E and F), indicating $\delta^{13}$C$_{POC}$ was related to the abundance of CO$_2$ and biological production in the western Arctic Ocean. Indeed, a significant negative correlation was observed between surface $\delta^{13}$C$_{POC}$ and log[$\text{CO}_2(\text{aq})$] (logarithmic values were adopted here after Popp et al. (1989) empirically) (Fig. 4). This indicated the dependence of the POC-$\delta^{13}$C composition on the aqueous CO$_2$ concentration in the western Arctic Ocean during summer, which could be described with the following relationship:

$$\delta^{13}C_{POC} = -9.19 - 12.75 \log[\text{CO}_2(\text{aq})] \quad (r^2 = 0.63, p < 0.0001)$$

This is the first time that such a negative correlation has been revealed in the western Arctic Ocean. Similar relations have been reported previously in other areas, such as the Indian Ocean (Francois et al., 1993), the Atlantic Ocean (Rau et al., 1992), the Southern Ocean (Fischer, 1991; Kennedy and Robertson, 1995; Lourey et al., 2004), the Antarctic seas (Rau et al., 1991), and model results in the world ocean (Hofmann et al., 2000).

When inorganic carbon acquisition is maintained only by passive CO$_2$ diffusion during plankton photosynthesis, the $\delta^{13}$C values of the POC produced can be expressed as a function of $\text{CO}_2(\text{aq})$ (Cullen et al., 2001; Hofmann et al., 2000; Laws et al., 1995; Rau et al., 1996):

$$\delta^{13}C_{POC} = \delta^{13}C_{CO_2(aq)} - \varepsilon f + a \frac{\mu}{[\text{CO}_2(\text{aq})]}$$

where $\delta^{13}C_{CO_2(aq)}$ is the $^{13}$C isotopic composition of the substrate $\text{CO}_2(aq)$, $\varepsilon f$ is the carbon isotopic fractionation associated with photosynthetic fixation, $\mu$ is the specific growth rate, and $a$ is a species-specific constant.

Although direct measurements of the $\delta^{13}$C composition of aqueous CO$_2$ were not carried out here, short-term changes in $\delta^{13}C_{CO_2(aq)}$ should not be a major factor responsible for the large variations in $\delta^{13}C_{POC}$ (up to 7%$_{o}$) observed in the study area. Globally, the $\delta^{13}$C value of surface ocean total dissolved CO$_2$ (DIC) does not vary greatly (Broecker and Maier-Reimer, 1992; Lynch-Stieglitz et al., 1995), while gradients in $\delta^{13}C_{POC}$ are much greater among different sea areas (Hofmann et al., 2000). Locally, the polar oceans have experienced very small changes in surface $\delta^{13}C_{POC}$ (< 3%$_{o}$) in recent decades compared with other regions (Quay et al., 2003), and the $\delta^{13}$C value of CO$_2$ in seawater in equilibrium with the atmosphere covaried with temperature, but at a slow rate (Mook et al., 1974). Thus, it is less likely that such a large variation in $\delta^{13}C_{POC}$ (up to 7%$_{o}$) observed in the western Arctic Ocean was mainly caused by changes in isotopic compositions of $\text{CO}_2(aq)$.

Our study demonstrated that $\delta^{13}$C$_{POC}$ in the western Arctic Ocean was controlled by the aqueous CO$_2$ concentration. However, some other studies have showed that $\delta^{13}$C$_{POC}$ could also vary independently of $[\text{CO}_2(\text{aq})]$, such as in the southeastern Bering Sea (Guo et al., 2004) and in some parts of the Southern Ocean (Bentaleb et al., 1998; Francois et al., 1993; Popp et al., 1999), indicating the influence of other factors on $\delta^{13}$C$_{POC}$. They may include the active uptake of bicarbonate (HCO$_3$$_{-}$, with the help of a carbon concentrating mechanism) (Cassar et al., 2004; Tortell et al., 1997), phytoplankton species composition (Cullen et al., 2001; Kopczynska et al., 1995; Rau et al., 1992), cell geometry (Burkhardt et al., 1999; Popp et al., 1998; Trull and Armand, 2001), and zooplankton-related processes (Rau et al., 1990; Tamelander et al., 2006). More studies are needed to further understand the ultimate controls on $\delta^{13}$C$_{POC}$. 

Fig. 3. Relationship between POC ($\mu$M) and Chl-a ($\mu$g/dm$^3$) in the western Arctic Ocean during summer 2003.

Fig. 4. Relationship between $\delta^{13}$C$_{POC}$ and log[$\text{CO}_2(\text{aq})$] in the western Arctic Ocean during summer 2003.
4.3. Possible effect of anthropogenic CO$_2$ on $\delta^{13}$CPOC

The invasion of isotopically “light” anthropogenic CO$_2$ into the upper ocean could result in both an increase in [CO$_2$(aq)] and a decrease in its $\delta^{13}$C, causing a subsequent decrease in $\delta^{13}$CPOC in the water column (Cullen et al., 2001; Druffel and Benavides, 1986; Quay et al., 2003, 1992; Schell, 2001). The concentration of atmospheric CO$_2$ has increased from ~280 to ~380 ppm since the Industrial Revolution (www.esrl.noaa.gov/gmd/ccgg/trends). Assuming the negative correlation between $\delta^{13}$CPOC and log[CO$_2$(aq)] observed in this study has held true over the past century or so, the following equation can be inferred:

$$\Delta \delta^{13}\text{CPOC} = -12.75 \Delta \log[\text{CO}_2(aq)]$$

If the surface seawater remains at a steady state where $T=0$ °C and $S=30$, then an overall decrease of about $-1.7\%$ in $\delta^{13}$CPOC can be estimated since preindustrial times. In other words, an average decrease in its $\delta^{13}$C has increased from 280 to ~380 ppm since the Industrial Revolution (www.esrl.noaa.gov/gmd/ccgg/trends). This decrease is comparable to the anthropogenic decrease rates of $\delta^{13}$C reported for global atmospheric CO$_2$ (Friedli et al., 1986) and surface ocean DIC (Druffel and Benavides, 1986; Quay et al., 1992; Quay et al., 2003). It is also similar to the fractionation in $\delta^{13}$C between modern POM and surface sediments in the Arctic Ocean (Bauch et al., 2000), but it is much lower than the observed decrease in planktonic $\delta^{13}$C in the Bering Sea in recent decades (Cullen et al., 2001; Schell, 2001). Although the overall change in $\delta^{13}$CPOC from the increase in anthropogenic CO$_2$ on seasonal and yearly time scales could be relatively small compared to the biological fractionation in $\delta^{13}$C and spatial changes in $\delta^{13}$CPOC, the long-term effect on $\delta^{13}$CPOC due to anthropogenic impacts should be detectable in the sediments, especially on decadal time scales.

5. Conclusions

Our results showed that $\delta^{13}$CPOC in the surface seawater generally decreased from the continental shelf to the deep basin in the western Arctic Ocean. $\delta^{13}$CPOC and photosynthetic carbon isotopic fractionation were related to the dissolved CO$_2$ concentration in surface waters. Biological processes were a major factor affecting surface water CO$_2$ concentrations and further controlling the variation of $\delta^{13}$CPOC. The significant correlation between $\delta^{13}$CPOC and dissolved CO$_2$ supports the use of $\delta^{13}$C as a proxy for carbon dynamics in the Arctic Ocean. Thus, signatures of $\delta^{13}$C in sediment core samples together with sediment chronologies should allow the reconstruction of changes in dissolved CO$_2$ of the surface ocean, if a functionally coupled relationship between $\delta^{13}$CPOC in the water column and $\delta^{13}$CPOC in the sediment can be established.

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