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# An isotopic perspective on the correlation of surface ocean carbon dynamics and sea ice melting in Prydz Bay (Antarctica) during austral summer

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## ABSTRACT

The stable carbon isotope composition of particulate organic carbon ( $\delta^{13}\text{C}_{\text{POC}}$ ) and naturally occurring long-lived radionuclide  $^{226}\text{Ra}$  ( $T_{1/2}=1600$  a) were applied to study the variations of upper ocean ( $< 100$  m) carbon dynamics in response to sea ice melting in Prydz Bay, East Antarctica during austral summer 2006. Surface  $\delta^{13}\text{C}_{\text{POC}}$  values ranged from  $-27.4\text{‰}$  to  $-19.0\text{‰}$  and generally decreased from inner bay (south of  $67^\circ\text{S}$ ) toward the Antarctic Divergence. Surface water  $^{226}\text{Ra}$  activity concentration ranged from  $0.92$  to  $2.09$   $\text{Bq/m}^3$  (average  $1.65 \pm 0.32$   $\text{Bq/m}^3$ ,  $n=20$ ) and increased toward the Antarctic Divergence, probably reflecting the influence of  $^{226}\text{Ra}$ -depleted meltwater and upwelled  $^{226}\text{Ra}$ -replete deep water. The fraction of meltwater,  $f_i$ , was estimated from  $^{226}\text{Ra}$  activity concentration and salinity using a three-component (along with Antarctic Summer Surface Water, and Prydz Bay Deep Water) mixing model. Although the fraction of meltwater is relatively minor ( $1.6$ – $11.9\%$ , average  $4.1 \pm 2.7\%$ ,  $n=20$ ) for the surface waters (sampled at  $\sim 6$  m), a positive correlation between surface  $\delta^{13}\text{C}_{\text{POC}}$  and  $f_i$  ( $\delta^{13}\text{C}_{\text{POC}}=0.94 \times f_i - 28.44$ ,  $n=20$ ,  $r^2=0.66$ ,  $p < 0.0001$ ) was found, implying that sea ice melting may have contributed to elevated  $\delta^{13}\text{C}_{\text{POC}}$  values in the inner Prydz Bay compared to the open oceanic waters. This is the first time for a relationship between  $\delta^{13}\text{C}_{\text{POC}}$  and meltwater fraction to be reported in polar oceans to our knowledge. We propose that sea ice melting may have affected surface ocean  $\delta^{13}\text{C}_{\text{POC}}$  by enhancing water column stability and providing a more favorable light environment for phytoplankton photosynthesis, resulting in drawdown of seawater  $\text{CO}_2$  availability, likely reducing the magnitude of isotope fractionation during biological carbon fixation. Our results highlight the linkage of ice melting and  $\delta^{13}\text{C}_{\text{POC}}$ , providing insights into understanding the carbon cycling in the highly productive Antarctic waters.

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## 1. Introduction

Stable carbon isotope composition of suspended particulate organic matter ( $\delta^{13}\text{C}_{\text{POC}}$ ) can potentially provide important insights into the environmental conditions under which carbon fixation occurs (Kennedy and Robertson, 1995; Laws et al., 1995; Lourey et al., 2004). This is mainly because marine phytoplankton preferentially assimilate the lighter isotope ( $^{12}\text{C}$ ) during photosynthetic uptake of aqueous carbon dioxide, making the stable carbon isotope composition of the residual pool of dissolved inorganic carbon more enriched in  $^{13}\text{C}$ . The understanding of key controlling factors on  $\delta^{13}\text{C}_{\text{POC}}$  may provide invaluable information for the interpretation of sedimentary organic  $\delta^{13}\text{C}$  signatures

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( $\delta^{13}\text{C}_{\text{org}}$ ), which has important implications for the reconstruction of paleo- $\text{CO}_2$  levels in surface ocean (Bentaleb et al., 1996; Freeman and Hayes, 1992; Jasper and Hayes, 1990).

The Southern Ocean comprises 20% of the total area of the world oceans and plays a crucial role on the global carbon cycling and climate change (Anderson and Carr, 2010; Caldeira and Duffy, 2000; Francois et al., 1997). In the high latitudes, the Antarctic waters are experiencing rapid changes (Meredith and King, 2005), where sea ice melting is one of the most prominent environmental driving forces during phytoplankton growth seasons (Smith and Nelson, 1985; Vernet et al., 2008). The concentrations of macronutrients are generally very high, and stratification has been viewed as a key physical forcing in regulating primary production in the Southern Ocean (Long et al., 2012; Nelson et al., 1989). The input of meltwater may change the stratification of the upper water column and thus the light availability to phytoplankton, which is usually considered a major limiting factor for phytoplankton growth in the Southern Ocean (Mitchell et al., 1991;

Mitchell and Holm-Hansen, 1991). As seawater density is much more sensitive to changes in salinity under low temperatures (Sigman et al., 2004), sea ice melting may exert great influence on the phytoplankton production (Smith and Nelson, 1985; Vernet et al., 2008). The stratification and shallow mixed layer depths (MLD) is of great importance in Antarctic waters in regard to formation of blooms (Mitchell and Holm-Hansen, 1991). Changes in primary production control the degree of biological drawdown of nutrients and CO<sub>2</sub> in surface waters and shape the product POC  $\delta^{13}\text{C}$  values. For example, lowered CO<sub>2</sub> availability will allow a decreased carbon isotope fractionation during carbon fixation and make the product POC more enriched in <sup>13</sup>C relative to <sup>12</sup>C (Zhang et al., 2012). Unfortunately, assessment of the relationship between  $\delta^{13}\text{C}_{\text{POC}}$  and the fraction of sea ice meltwater in surface waters has been hindered by the fact that these two variables have rarely been measured simultaneously in field studies, while such relationship may provide important implications for understanding the past, present, and future climate change.

We have thus attempted to obtain patterns of covariance between  $\delta^{13}\text{C}_{\text{POC}}$  and the fraction of sea ice meltwater by collecting samples in Prydz Bay, East Antarctica, where a pronounced [CO<sub>2</sub>(aq)] gradient has been reported (Gao et al., 2008), and concurrently measuring primary production. Our hypothesis is that there should be a positive correlation between  $\delta^{13}\text{C}_{\text{POC}}$  and the fraction of sea ice meltwater in surface waters in Prydz Bay during austral summer, as the availability of nutrients/CO<sub>2</sub> and primary production may all be regulated by changes in surface ocean stratification in this region. This study could provide unique insights into the physical–biological coupling of surface ocean carbon dynamics in the high-latitude waters.

## 2. Methods

### 2.1. Study area

Prydz Bay is a triangular-shaped embayment covering an area of ~80,000 km<sup>2</sup> in the Indian sector of Southern Ocean (Stagg,

1985). It is one of the three major Antarctic embayments (the other two are Weddell Sea and Ross Sea). It is located between the West Ice Shelf (around 80°E) and Cape Darnley (70°E) and the region off the Mawson coast which is often ice-covered. Surface circulation in Prydz Bay is characterized by a closed cyclonic gyre adjacent to the Amery Ice Shelf, and there is inflow of cold water from the east near the West Ice Shelf and outflow near Cape Darnley (Smith et al., 1984; Wong, 1994). Outside, the west drift dominates northward of 63°S and the east drift dominates southward of 65°S. The transition zone between the west and east drifts locates the Antarctic Divergence with the strong upwelling of Circumpolar Deep Water due to the shearing stress forced by wind (Gao et al., 2008). During austral summer, the surface waters in Prydz Bay can be composed of three components: Antarctic Surface Water, Prydz Bay Intermediate/Deep Water, and sea ice meltwater (Le et al., 1998; Pu et al., 2000; Smith et al., 1984).

During the 22nd Chinese Antarctic Research Expedition (CHINARE) cruise aboard the icebreaker R/V Xuelong, a total of 24 stations in the Prydz Bay region (68°E–76°E, 64°S–70°S) were sampled from 16 to 24 January 2006 (Table 1 and Fig. 1). It is the late period for sea ice melting in Prydz Bay (Zheng, 2011), and the study area was generally ice free during our sampling period as observed from the Advanced Microwave Scanning Radiometer for Earth Observing System (AMSR-EOS) daily satellite sea ice images (<http://www.iup.uni-bremen.de:8084/amr/amr.html>; Spreen et al., 2008). During the cruise, environmental parameters (temperature, salinity and macronutrient concentration) were measured. <sup>226</sup>Ra activity concentrations were measured to estimate the fraction of meltwater.  $\delta^{13}\text{C}_{\text{POC}}$  and primary production were measured to provide the information for the evaluation of physical–biological coupling with respect to ice melting.

### 2.2. Temperature, salinity and macronutrient concentrations

Water temperature and salinity (S) were recorded using a CTD system, while samples for macronutrient samples were collected from discrete depths (0, 25, 50, 100 m) using 10-L Niskin bottles,

**Table 1**

Sampling locations, surface seawater temperature, salinity, surface mixed layer depth (MLD), water mass fraction ( $f_i$ : meltwater;  $f_a$ : Antarctic Surface Water;  $f_p$ : Prydz Bay Intermediate/Deep Water) and primary production in Prydz Bay during January 2006. Measurements of <sup>226</sup>Ra activity concentration and the estimation of water mass fraction were conducted for water samples collected from ~6 m.

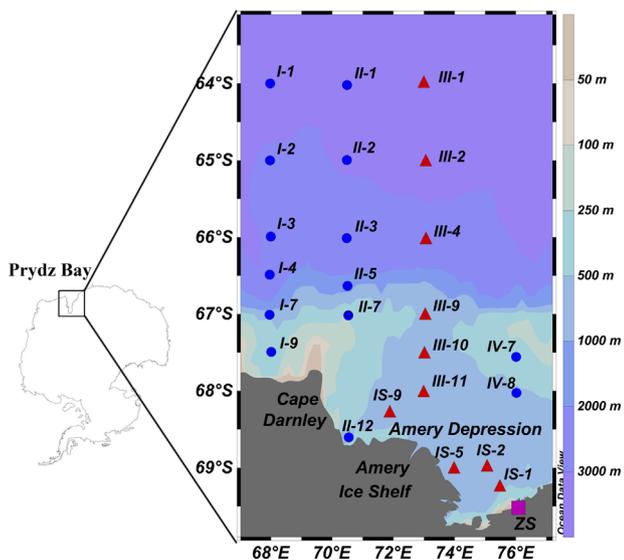
Station	Longitude (°E)	Latitude (°S)	T (°C)	S	MLD (m)	<sup>226</sup> Ra (mean ± 1σ) (Bq/m <sup>3</sup> )	$f_i$ (%)	$f_a$ (%)	$f_p$ (%)	PP (mmolC/m <sup>3</sup> /d)
IS-1	75.45	69.25	2.59	32.994	29	1.61 ± 0.04	5.4	42.3	52.3	nd
IS-2	75.00	69.00	3.41	33.032	3	1.99 ± 0.04	5.2	60.7	34.1	5.3
IS-5	74.00	69.00	1.54	31.060	1	0.92 ± 0.03	11.9	10.7	77.4	nd
IS-9	71.85	68.28	-1.23	33.733	9	nd	nd	nd	nd	nd
I-9	68.00	67.50	-0.89	32.522	30	1.22 ± 0.03	7.0	23.9	69.1	2.8
II-7	70.53	67.00	-0.30	32.217	8	nd	nd	nd	nd	1.8
II-12	70.52	68.63	0.96	33.134	17	1.16 ± 0.03	5.1	20.4	74.5	1.7
III-9	73.00	67.01	-0.58	33.723	1	nd	nd	nd	nd	nd
III-10	72.99	67.53	1.11	31.931	5	1.74 ± 0.04	8.8	49.7	41.5	2.2
III-11	73.00	68.02	3.83	33.379	10	1.59 ± 0.04	4.2	41.0	54.8	3.9
IV-7	75.97	67.57	0.13	32.057	12	nd	nd	nd	nd	nd
IV-8	76.01	68.01	2.65	33.113	16	1.71 ± 0.04	5.0	47.1	47.9	nd
I-1	67.98	64.00	0.58	33.719	37	1.95 ± 0.04	3.0	58.1	38.9	1.1
I-2	67.99	65.00	0.93	33.845	47	1.89 ± 0.04	2.6	55.1	42.3	1.1
I-3	68.00	66.00	0.92	34.037	37	1.36 ± 0.03	2.1	29.2	68.7	1.1
I-4	68.00	66.50	0.85	34.009	42	2.09 ± 0.04	2.0	64.7	33.4	1.8
I-7	68.00	67.00	0.88	33.964	32	1.93 ± 0.04	2.2	56.9	40.9	1.6
II-1	70.51	64.00	0.93	33.748	27	2.00 ± 0.04	2.8	60.5	36.6	2.0
II-2	70.51	65.00	1.72	33.956	43	1.61 ± 0.03	2.3	41.4	56.3	2.0
II-3	70.50	66.00	1.11	33.966	38	1.71 ± 0.04	2.2	46.3	51.5	2.3
II-5	70.50	66.66	1.27	33.231	17	1.40 ± 0.03	4.7	31.9	63.4	1.9
III-1	73.00	63.97	0.92	33.908	29	1.80 ± 0.04	2.4	50.7	46.9	2.2
III-2	73.01	65.01	0.72	34.132	39	1.90 ± 0.04	1.6	55.3	43.0	1.9
III-4	73.03	66.01	1.17	34.075	20	1.46 ± 0.03	1.9	34.1	64.0	1.1

Note: nd represents no data.

consistent with previous CHINARE cruises. Nitrate concentrations were determined by the standard pink azo dye method, while phosphate and silicate were determined by the standard molybdenum blue method (Hansen and Koroleff, 1999) onboard immediately after seawater sampling and filtration through 0.45  $\mu\text{m}$  cellulose acetate membrane. Nutrient measurements were not conducted at the stations IS-1, IS-5, and IS-9 in the vicinity of the Amery Ice Shelf. Both the CTD and nutrient data are provided by the CHINARE program ([www.polar.gov.cn](http://www.polar.gov.cn)).

### 2.3. Fraction of meltwater ( $f_i$ )

The naturally occurring long-lived uranium-series nuclide,  $^{226}\text{Ra}$  ( $T_{1/2}=1600\text{ a}$ ), is an effective tracer of water mixing (Ku and Luo, 1994; van Beek et al., 2008) and was employed in this study to estimate the fraction of meltwater. Due to the continuous input from the bottom sediments via the decay of  $^{230}\text{Th}$ , the deep waters generally have higher  $^{226}\text{Ra}$  activity concentrations, which decrease upward due to water mixing (Annett et al., 2013; Ku et al., 1970; Ku and Luo, 1994). Relative to the oceanic waters, the sea ice and its meltwater is depleted in  $^{226}\text{Ra}$  activity concentration as a result of the exclusion of salts during freezing process (Xing et al., 2003). The large difference between the meltwater and the oceanic waters make the estimation of sea ice meltwater fraction from  $^{226}\text{Ra}$  and salinity measurements feasible in the Antarctic waters.



**Fig. 1.** Map showing the sampling stations during the 2006 CHINARE cruise in Prydz Bay. The red triangles represent the vertically-sampled stations, and blue circles represent the surface-sampled stations. The purple rectangle represents the Chinese Antarctic Zhongshan Station (ZS). The station prefix IS represents the Amery Ice Shelf, while I, II, III and IV represents the transects at 68°S, 71°S, 73°S, and 76°S, respectively. Contours refer to bathymetry (in meters). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

#### 2.3.1. $^{226}\text{Ra}$ and salinity endmember values

The  $^{226}\text{Ra}$  and salinity endmember values of the oceanic water masses (Antarctic Surface Water and Prydz Bay Intermediate/Deep Water) are cited from references (Hanfland, 2002; Ku et al., 1970; Ku and Lin, 1976) and listed in Table 2. The sea ice endmember values were obtained from measurements in this study. Briefly, previous studies have shown that the Antarctic Surface Water has mean  $^{226}\text{Ra}$  activity concentration of  $2.83\text{ Bq/m}^3$  (Chung, 1987; Hanfland, 2002; Ku et al., 1970; Ku and Lin, 1976). Assuming that the sediments are the major source of  $^{226}\text{Ra}$  to the overlying seawater column and we treat Prydz Bay Intermediate/Deep Water as one, we can derive the  $^{226}\text{Ra}$  endmember value from the  $^{226}\text{Ra}$  activity concentration at the layer closest to the seafloor (mean  $3.60\text{ Bq/m}^3$ ) minus the surface seawater value of  $2.83\text{ Bq/m}^3$  (Hanfland, 2002; Ku et al., 1970; Ku and Lin, 1976). The reported high limit (either summer or winter) salinity of 34.50 (excluding the effect of meltwater dilution) is chosen as the endmember value for the Antarctic Surface Water (Le et al., 1998; Pu et al., 2000). The average salinity (34.72) of the Circumpolar Deep Water and Antarctic Bottom Water has been chosen as the feature salinity for the Prydz Bay Intermediate/Deep Water (Chen et al., 2005; Chen et al., 1995; Le et al., 1998).

#### 2.3.2. $^{226}\text{Ra}$ measurement

Seawater samples ( $\sim 140\text{ L}$ ) for  $^{226}\text{Ra}$  measurement were collected at 20 stations using a submersible pump equipped at  $\sim 6\text{ m}$  below sea surface. To determine  $^{226}\text{Ra}$  activity concentration of the sea ice endmember, sea ice samples were collected at around  $69^\circ\text{S}$ ,  $76.3^\circ\text{E}$  and melted together under room temperature. The method for  $^{226}\text{Ra}$  measurements is after Xie et al. (1994). Water samples were then concentrated by passing through a column with 12 g  $\text{MnO}_2$ -fiber. Flow rate of  $200\text{--}250\text{ cm}^3/\text{min}$  was used in order to adsorb radium isotopes efficiently. After the enrichment,  $\text{MnO}_2$ -fiber was taken out and enveloped in a plastic bag while on the sea.  $^{226}\text{Ra}$  activity was measured by the  $^{222}\text{Rn}$  emanation method in the land laboratory. In brief,  $\text{MnO}_2$ -fiber was placed in a diffusion tube, sealed and vacuumized. After 5–7 d, the diffusion tube was connected to a vacuumized scintillation counting cell and  $^{222}\text{Rn}$  was emanated into the ZnS counting cell. Being sealed in the cell for 3 h,  $^{222}\text{Rn}$  will be in equilibrium with its daughters. The activities were subsequently measured on an Rn–Th analyzer (FD-125, Beijing Nuclear Instrument Factory). The precision ( $1\sigma$ ) based on duplicate analyses was within  $\pm 10\%$ .

#### 2.3.3. Estimation of $f_i$

The mass balance ( $^{226}\text{Ra}$  and salinity) equations for the surface waters in the study area are as follows:

$$f_i + f_a + f_p = 1 \quad (1)$$

$$f_i S_i + f_a S_a + f_p S_p = S_m \quad (2)$$

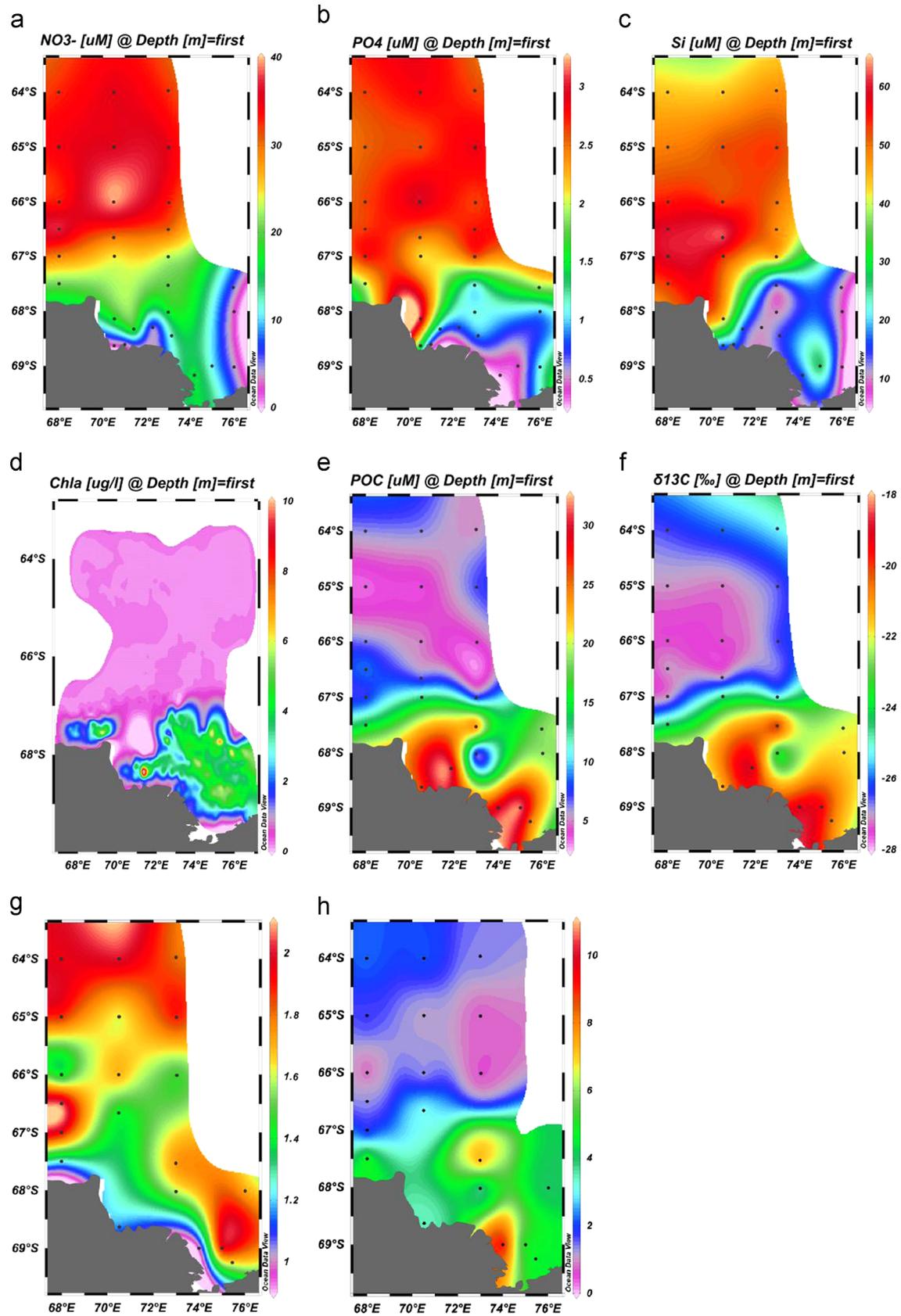
$$f_i A_i + f_a A_a + f_p A_p = A_m \quad (3)$$

where  $f$ ,  $S$ , and  $A$  represent the fraction, salinity and  $^{226}\text{Ra}$  activity concentration for each water mass ( $i$ =meltwater;  $a$ =Antarctic

**Table 2**

$^{226}\text{Ra}$ -Salinity endmember values of the water masses.  $^{226}\text{Ra}$  activity concentration ( $\text{Bq/m}^3$ ) and salinity in sea ice meltwater were measured in this study.

	Antarctic surface water	Prydz Bay intermediate/deep water	Meltwater	Reference
Salinity	34.56	34.72	4.00	Smith et al., 1984; Pu et al., 2000; Le et al., 1998; Chen et al., 1995; Chen et al., 2005; This study
$^{226}\text{Ra}$ ( $\text{Bq/m}^3$ )	2.83	0.77	0.17	Ku et al., 1970; Ku et al., 1976; Chung, 1987; Hanfland 2002; This study



**Fig. 2.** Distribution of surface seawater (a)  $[\text{NO}_3^-]$  ( $\mu\text{M}$ ), (b)  $[\text{PO}_4^{3-}]$  ( $\mu\text{M}$ ), (c)  $[\text{Si}(\text{OH})_4]$  ( $\mu\text{M}$ ), (d) chlorophyll a ( $\mu\text{g/L}$ ), (e) POC concentration ( $\mu\text{M}$ ), (f)  $\delta^{13}\text{C}_{\text{POC}}$  ( $\text{‰}$ ), (g)  $^{226}\text{Ra}$  activity concentration ( $\text{Bq/m}^3$ ), and (h) fraction of meltwater (%) in Prydz Bay (January 17–24, 2006). Chlorophyll data were cited from the Moderate Resolution Imaging Spectroradiometer (MODIS) Aqua satellite data archive (<http://oceanwatch.pifsc.noaa.gov:8080/thredds/dodsc/aqua/>).

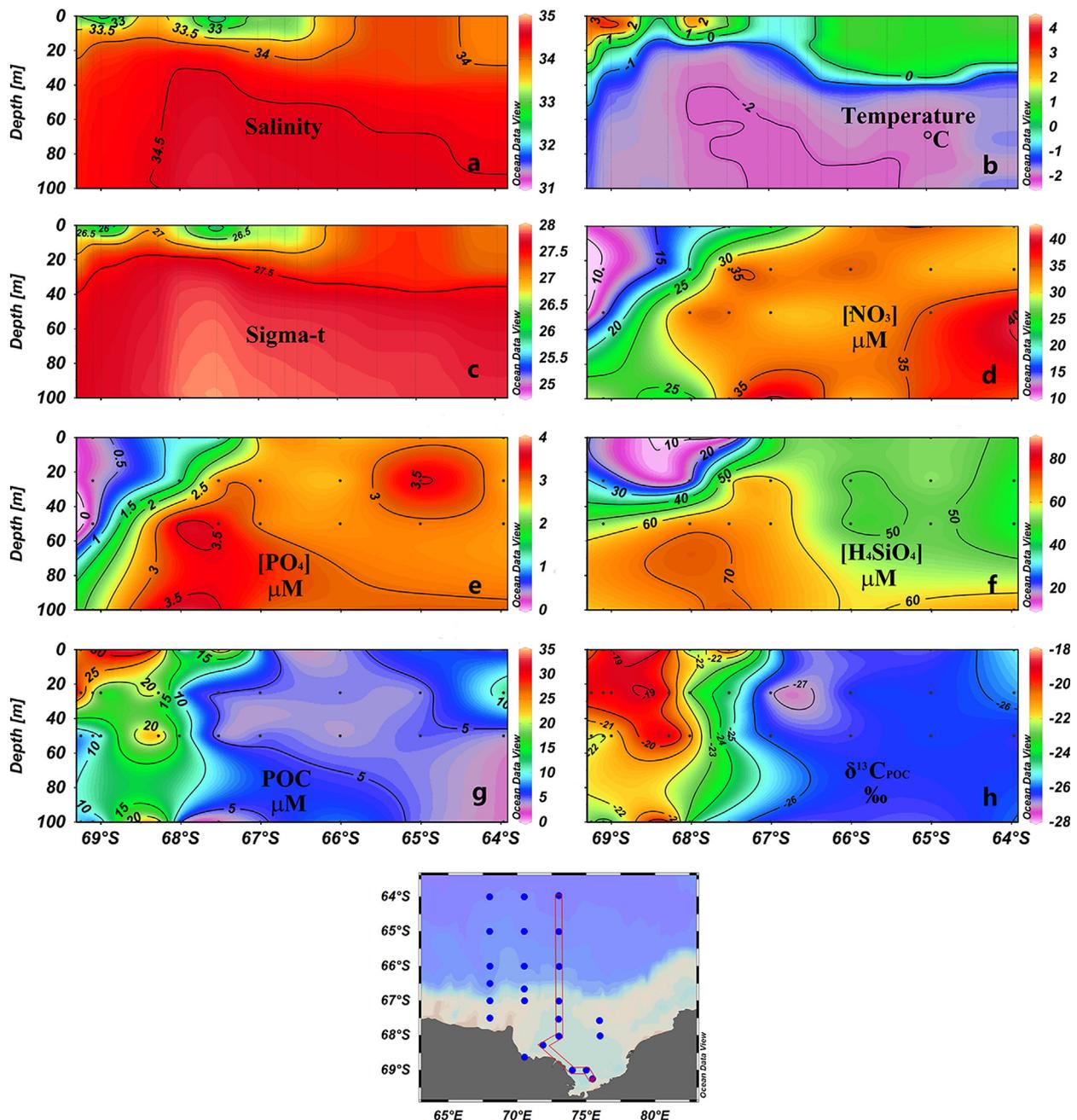


Fig. 3. Depth profiles of (a) salinity, (b) temperature, (c) density, (d)  $[\text{NO}_3^-]$ , (e)  $[\text{PO}_4^{3-}]$ , (f)  $[\text{Si}(\text{OH})_4]$ , (g) POC concentration, and (h)  $\delta^{13}\text{C}_{\text{POC}}$  in the upper 100 m along 73°E. The pathway of the transect is shown at the bottom.

Surface Water; *p*=Prydz Bay Intermediate/Deep Water; *m*=measured values), respectively.

#### 2.4. POC concentration and $\delta^{13}\text{C}_{\text{POC}}$

Seawater samples for POC concentration and  $\delta^{13}\text{C}_{\text{POC}}$  analyses were collected using Niskin bottles from four depths (0, 25, 50, 100 m) at 10 stations, while for the other 14 stations, only surface (0–5 m) was sampled (Fig. 1). About 2.0 L seawater was filtered through a precombusted (400 °C, 4 h) Whatman GF/F (pore size 0.7 μm) membrane. The membranes were dried (60 °C) before being stored frozen while on the sea. In land laboratory, the filter was decarbonated by wetting with Milli-Q water and fuming with HCl overnight prior to analysis. After being dried (60 °C) the

samples were then wrapped into tin capsules for measurements of POC concentration and its  $^{13}\text{C}$  abundance on a Thermo Finnigan MAT DELTA<sup>plus</sup> XP isotope ratio mass spectrometer coupled with a Carlo Erba NC2500 elemental analyzer (EA-IRMS). Pure tank  $\text{CO}_2$  calibrated on the VPDB scale against the reference standards IAEA-C-8 of the International Atomic Energy Agency and GBW04407 (black charcoal, –22.4‰VPDB) of National Standards of the People's Republic of China was used as a working standard.

The stable carbon isotopic compositions in suspended POC samples are presented in the delta per mil notation versus V-PDB (‰ VPDB):

$$\delta^{13}\text{C} = \left( \frac{R_{\text{Sample}}}{R_{\text{Standard}}} - 1 \right) \times 1000 \quad (4)$$

where  $R_{\text{Sample}}$  and  $R_{\text{Standard}}$  represent the  $^{13}\text{C}/^{12}\text{C}$  ratios of sample and the standard, respectively. The precision of  $\delta^{13}\text{C}$  measurements was within  $\pm 0.2\%$ .

### 2.5. Primary production

Primary production was measured at 18 stations from the sum of nitrate uptake (new production) and ammonium uptake (regenerated production) using  $^{15}\text{N}$  techniques (Dugdale and Wilkerson, 1986). First, about 2.0 L seawater was filtered through a precombusted (400 °C, 4 h) Whatman GF/F (pore size 0.7  $\mu\text{m}$ ) membrane to collect natural (non-incubated) PON samples. As for the  $^{15}\text{N}$  uptake rate experiment, water samples were poured into two 1 L transparent glass bottles amended either with  $^{15}\text{NO}_3^-$  or  $^{15}\text{NH}_4^+$  (98.5  $^{15}\text{N}$  atom%) at a level of  $\sim 10\%$  ambient concentrations. The bottles were then incubated for 24 h under natural light level in a deck incubator, in which the temperature was maintained by a continuous flow of pumped surface seawater. The incubation was terminated by filtering onto precombusted (400 °C, 4 h) Whatman GF/F membranes (pore size 0.7  $\mu\text{m}$ ). PON concentration ( $\mu\text{M}$ ) and its  $^{15}\text{N}$  abundance were measured on the EA-IRMS. Pure tank  $\text{N}_2$  calibrated against the reference standards IAEA-N-1 and IAEA-N-3 was used as a working standard. The precision of  $\delta^{15}\text{N}$  measurements was within  $\pm 0.2\%$ .

The absolute uptake rate ( $\rho$ ,  $\text{mmolN}/\text{m}^3/\text{d}$ ) for either  $\text{NO}_3^-$  or  $\text{NH}_4^+$  uptake is calculated using a constant specific uptake model (Dugdale and Wilkerson, 1986):

$$\rho = \ln \frac{^{15}\text{N}_{\text{enr}} - ^{15}\text{N}_{\text{natur}}}{^{15}\text{N}_{\text{enr}} - ^{15}\text{N}_s} \times [\text{PON}_s] \quad (5)$$

where  $^{15}\text{N}_{\text{enr}}$ ,  $^{15}\text{N}_{\text{natur}}$ , and  $^{15}\text{N}_s$  are the absolute  $^{15}\text{N}$  abundances ( $^{15}\text{N}$  atom%) for the DIN pool at the beginning of incubation, natural PON sample, and the final  $\text{PON}_s$ , respectively. Primary production ( $\text{mmolC}/\text{m}^3/\text{d}$ ) is calculated by converting the sum of  $\rho\text{NO}_3$  and  $\rho\text{NH}_4$  after Redfield ratio ( $\Delta\text{C}/\Delta\text{N}=106/16$ ). Such Redfield stoichiometry has been confirmed to hold true in the growth season in Prydz Bay (Gibson and Trull, 1999).

## 3. Results

### 3.1. Hydrographic features

The surface waters north of 67°S were characterized by higher salinity and nutrient concentrations compared with the region south of 67°S (Table 1, Figs. 2 and 3). Surface seawater temperature (SST) north of 67°S varied around  $1.05 \pm 1.21$  °C (Table 1). Generally lower SSS in the southern surface waters indicated an increased contribution of freshwater input via ice melting. SST was higher in the Amery Depression, likely suggesting the effect of prolonged solar heating in the polynya (Pu et al., 2010). Macro-nutrient concentrations in the surface layer were generally lower in the inner Prydz Bay area (Fig. 2a–c), indicating significant biological depletion. Spatial coherence of seawater salinity and temperature with density ( $\sigma_t$ ) clearly showed that the release of meltwater has changed the density field for the upper 100 m along 73°E (Fig. 3a–c).

### 3.2. $^{226}\text{Ra}$ activity concentration

Surface water  $^{226}\text{Ra}$  activity concentration ranged between 0.92 and 2.09  $\text{Bq}/\text{m}^3$  (average  $1.65 \pm 0.32$   $\text{Bq}/\text{m}^3$ ,  $n=20$ ) (Table 1, Fig. 2g), generally falling in previous reported range in this area (Yin et al., 2004).  $^{226}\text{Ra}$  activity concentration increased northward, reflecting the decreased influence of ice meltwater relative to the  $^{226}\text{Ra}$ -rich Circumpolar Deep Water which upwelled around

64°S. Sea ice samples were depleted in  $^{226}\text{Ra}$  ( $A_i=0.17 \pm 0.03$   $\text{Bq}/\text{m}^3$ ), as well as low salinity (salinity=4). This is also confirmed by the results of 26th CHINARE cruise in Prydz Bay during austral summer 2009–2010 (He, 2012). The values were adopted as the endmember feature of meltwater in this study.

### 3.3. Fraction of meltwater ( $f_i$ )

Fraction of meltwater ( $f_i$ ) at  $\sim 6$  m ranged from 1.6% to 11.9% and averaged 4.1% ( $n=20$ ; Table 1 and Fig. 2h). Such values fall in the range of the published results (average 3.9%) using hydrogen isotope ( $\delta\text{D}$ ) approach in Prydz Bay during austral summer 1996–1997 (Cai et al., 2003). Although meltwater is not a major water mass compared to either Antarctic Surface Water ( $44.0 \pm 14.9\%$ ) or Prydz Bay Intermediate/Deep Water ( $51.9 \pm 13.7\%$ ) (Table 1), input of low-salinity waters will dramatically change the upper water column density field.  $f_i$  in the area north of 67°S was generally low ( $\sim 2\%$ ), while it increased dramatically southward.

### 3.4. POC concentration and $\delta^{13}\text{C}_{\text{POC}}$

POC concentration was relatively low (3.4–8.9  $\mu\text{M}$ ) in surface waters north of  $\sim 67^\circ\text{S}$  and increased remarkably southward from  $\sim 67^\circ\text{S}$ , reaching the maximum (32.4  $\mu\text{M}$ ) in the vicinity of the Amery Ice Shelf (Fig. 2e). Such an evident N–S gradient of surface POC concentration is in agreement with the results of phytoplankton cell abundance for this cruise in Prydz Bay (Zhu et al., 2007) and satellite-derived chlorophyll a distribution (Fig. 2d), implying an intensive phytoplankton bloom was occurring in the waters south of 67°S. Surface POC concentration was significantly correlated to phytoplankton (predominated by diatoms *Fragilariopsis kerguelensis* and *Fragilariopsis curta*) cell abundance (Zhu et al., 2007) and dissolved oxygen (data not shown; www.polar.gov.cn), adding to the point that POC was mainly produced in situ by phytoplankton.

Surface  $\delta^{13}\text{C}_{\text{POC}}$  values ranged between  $-19.0\%$  and  $-27.4\%$  (arithmetic mean of  $-24.3\%$ ,  $n=24$ ) and showed an increasing trend southward (Fig. 2f). Surface  $\delta^{13}\text{C}_{\text{POC}}$  values north of 67°S fell in a relatively narrow range of  $-25.3\%$  and  $-27.5\%$  (arithmetic mean of  $-26.8\%$ ,  $n=12$ ). Although temperatures were still low, more enriched  $\delta^{13}\text{C}_{\text{POC}}$  values ( $\delta^{13}\text{C}_{\text{POC}} > -22.0\%$ ) along with higher POC concentration toward the inner Prydz Bay was evident. Maximum  $\delta^{13}\text{C}_{\text{POC}}$  values ( $-19.9 \pm 1.0\%$ ,  $n=5$ ) were observed in the vicinity of the Amery Ice Shelf. Similarly,  $\delta^{13}\text{C}_{\text{POC}}$  in the upper 100 m along 73°E was distinctly higher south of 67°S, while it varied little north of 67°S (Fig. 3h). The most-enriched  $\delta^{13}\text{C}_{\text{POC}}$  values along with high POC concentrations along 73°E were generally observed at the station IS-9 throughout the upper 100 m.

### 3.5. Primary production

Surface primary production (PP) fell in a range of 1.1–5.3  $\text{mmolC}/\text{m}^3/\text{d}$  and averaged 2.1  $\text{mmolC}/\text{m}^3/\text{d}$  (Table 1), consistent with the reported range in Prydz Bay (Liu et al., 2004; Liu and Cai, 2002; Liu et al., 2001; Liu et al., 1997; Ning et al., 1993; Qiu et al., 2004). Primary production in south of 67°S ( $3.2 \pm 1.4$   $\text{mmolC}/\text{m}^3/\text{d}$ ,  $n=5$ ) was about twice of that north of 67°S ( $1.7 \pm 0.4$   $\text{mmolC}/\text{m}^3/\text{d}$ ,  $n=13$ ), confirming that the inner Prydz Bay is a much more favorable environment for phytoplankton growth. The distribution pattern is also consistent with that of chlorophyll a (Fig. 2d).

## 4. Discussion

### 4.1. Variations in $\delta^{13}\text{C}_{\text{POC}}$

$\delta^{13}\text{C}_{\text{POC}}$  data in Prydz Bay are scarce to date (Gibson et al., 1999; Kopczynska et al., 1995). However, a similar N–S spatial difference for  $\delta^{13}\text{C}_{\text{POC}}$  collected from subsurface (15 m and 60 m) has been reported (Kopczynska et al., 1995). When compared with published results in other areas in the high-latitude Southern Ocean, our  $\delta^{13}\text{C}_{\text{POC}}$  values north of  $67^\circ\text{S}$  ( $-26.8 \pm 0.6\text{‰}$ ,  $n=12$ ) are consistent with the low  $\delta^{13}\text{C}_{\text{POC}}$  values commonly observed in those open oceanic waters (Kennedy and Robertson, 1995; Kopczynska et al., 1995; Rau et al., 1991; Rau et al., 1989; Raven and Farquhar, 1990; Villinski et al., 2000). The relatively high  $\delta^{13}\text{C}_{\text{POC}}$  values in the inner Prydz Bay were also close to the reported values in other marginal ice zones in the Antarctic waters (Cozzi and Cantoni, 2011; Henley et al., 2012).

The relatively large  $\delta^{13}\text{C}_{\text{POC}}$  variations ( $\sim 8.0\text{‰}$ ) among stations observed in this study possibly reflects the effects of different surface water  $\text{CO}_2$  concentrations ( $[\text{CO}_2(\text{aq})]$ ) (O'Leary et al., 2001; Popp et al., 1999). Although  $[\text{CO}_2(\text{aq})]$  data for this cruise are not available due to technical error, previous CHINARE cruises (like in January from 1992–2000) in Prydz Bay have confirmed that the area south of  $67^\circ\text{S}$  generally acts as a strong  $\text{CO}_2$  sink, as featured by  $\Delta\text{pCO}_2$  (partial pressure of  $\text{CO}_2$  in seawater minus that in the overlying atmosphere) up to  $-100 \mu\text{atm}$  (Gao et al., 2008). By contrast, the area north of  $67^\circ\text{S}$  acts as a weak  $\text{CO}_2$  source, with seawater  $\text{pCO}_2$  slightly higher than that of atmosphere ( $\Delta\text{pCO}_2 \approx 5 \mu\text{atm}$ ) (Gao et al., 2008; Wang et al., 1998; Zhang et al., 1997). Indeed, negative correlations of surface seawater  $\text{pCO}_2$  versus either primary production, chlorophyll a, or phytoplankton cell abundance have been reported in previous CHINARE cruises in Prydz Bay (Liu et al., 2004; Liu and Cai, 2002), suggesting that biological uptake may dramatically drawdown surface water  $\text{CO}_2$  concentration in summer. This idea is also consistent with the results of a time-series study in the coastal Prydz Bay (Gibson and Trull, 1999).

$\delta^{13}\text{C}_{\text{POC}}$  values were positively correlated to POC concentration in the upper 100 m (Fig. 4), indicating a biomass effect as the dominant factor in shaping  $\delta^{13}\text{C}_{\text{POC}}$ , and possibly the changed magnitude of isotope fractionation during carbon fractionation. Briefly, lowered carbon isotope fractionation under decreased  $\text{CO}_2$  availability will cause elevated  $^{13}\text{C}/^{12}\text{C}$  ratios in POC. This hypothesis is supported by the negative correlation of surface  $\delta^{13}\text{C}_{\text{POC}}$  values to salinity-normalized nutrient concentrations (relative to salinity of 34.50, approximately the mean salinity of the upper

100 m in Prydz Bay during the cruise) (Fig. 5). These results suggest that  $\delta^{13}\text{C}_{\text{POC}}$  values were elevated with enhanced nutrient drawdown and probably concurrent lowered seawater  $\text{pCO}_2$ , as Redfield C/N uptake ratio for phytoplankton has been confirmed in Prydz Bay (Gibson and Trull, 1999). Thus, variations in  $\delta^{13}\text{C}_{\text{POC}}$  should have been imprinted with changes in key environmental conditions.

### 4.2. Correlation of $\delta^{13}\text{C}_{\text{POC}}$ and meltwater: physical–biological coupling

We propose that the recent ice melting-induced changes in surface ocean density field may be largely responsible for the elevated  $\delta^{13}\text{C}_{\text{POC}}$  values, where ice melting resulted in surface mixed layers that were both much shallower and more strongly stratified south of  $67^\circ\text{S}$  relative to the open oceanic waters (Fig. 3). Surface  $\delta^{13}\text{C}_{\text{POC}}$  values were positively correlated to the fraction of meltwater ( $\delta^{13}\text{C}_{\text{POC}} = 0.94 \times f_i - 28.44$ ,  $n=20$ ,  $r^2=0.66$ ,  $p < 0.0001$ ; Fig. 6), implying that as ice melting contributes relatively larger fractions of the surface waters, surface POC pool becomes more enriched in  $^{13}\text{C}$ . Although it has long been recognized that there exists a tight link between ice conditions and surface ocean carbon dynamics (Arrigo et al., 2008; Cai et al., 2010), this is the first time such a relationship between  $\delta^{13}\text{C}_{\text{POC}}$  and meltwater fraction to be reported in polar oceans to the best of our knowledge.

As a measure of the upper ocean stratification, surface mixed layer depth (MLD, here defined at the maximum of the buoyancy frequency, i.e., Brunt–Väisälä frequency, of the water column from  $\sigma_t$  profiles) has been recognized to play a key role in controlling physical and biological processes related to carbon dynamics in the Southern Ocean (Boyd, 2002; Mitchell et al., 1991). MLDs north of  $67^\circ\text{S}$  were generally deep (average of 34 m, Table 1) owing to both strong wind stress and circumpolar current. The wind and sea current make a less stable water column which is not favorable for either phytoplankton growth or POC accumulation (Mitchell and Holm-Hansen, 1991; Smith and Nelson, 1986). Surface POC and chlorophyll a concentrations north of  $67^\circ\text{S}$  were generally lower ( $\text{POC} \sim 5 \mu\text{M}$ ,  $\text{Chl-a} < 0.2 \text{ mg/m}^3$ ; Fig. 2 and Fig. 3). By comparison, ice melting-introduced low-salinity water created a more stable water column (MLD  $< 20$  m) in the inner Prydz Bay, as evidenced by a negative correlation between MLD and  $f_i$  (at  $\sim 6$  m):  $\text{MLD (m)} = -3.9 \times f_i (\%) + 41.8$ ,  $n=20$ ,  $r^2=0.53$ ,  $p < 0.001$ .

The balance between uptake and supply defines the extent of aqueous  $\text{CO}_2$  drawdown and probably the  $\delta^{13}\text{C}_{\text{POC}}$  variations in Prydz Bay, while MLD may have modulated both biological uptake and air–sea gas transfer. Reported air–sea  $\text{CO}_2$  flux in Prydz Bay during January generally fell in a range of  $0.6 \text{ mmolC/m}^2/\text{d}$  (open oceanic water as a weak  $\text{CO}_2$  source to the atmosphere) and  $-3.2 \text{ mmolC/m}^2/\text{d}$  (inner Prydz Bay as a  $\text{CO}_2$  sink to the atmosphere) from past CHINARE cruises (Gao et al., 2008; Wang et al., 1998; Zhang et al., 1997). When compared with the estimated depth-integrated primary production (integrated to 50 m, assuming carbon fixation rate at 50 m is negligible) for this cruise ( $27\text{--}133 \text{ mmolC/m}^2/\text{d}$ , average  $53 \text{ mmolC/m}^2/\text{d}$ ), it is clear that air–sea transfer of  $\text{CO}_2$  is insufficient to offset the biological uptake in the inner Prydz Bay. This idea is further corroborated by the finding that when urea uptake is taken into account, it may elevate the estimate of primary production by a level of  $\sim 10\%$  as shown by a study conducted also in Prydz Bay during February 2006 (Mohan et al., 2009). Moreover, past studies of CHINARE cruises (1999–2005) showed that surface seawater  $\text{pCO}_2$  values were negatively correlated with Chl-a in the Prydz Bay region but showed relatively little correlation with respect to SST (Chen et al., 2011). It is thus inferred that biological uptake should be the major factor (rather than temperature) controlling surface water  $\text{pCO}_2$  during austral summer in Prydz Bay. Surface primary

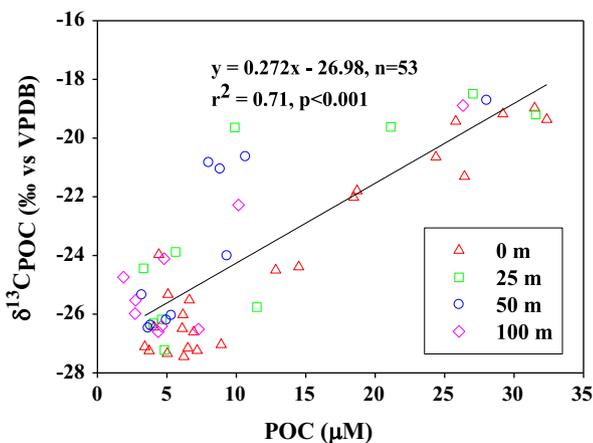
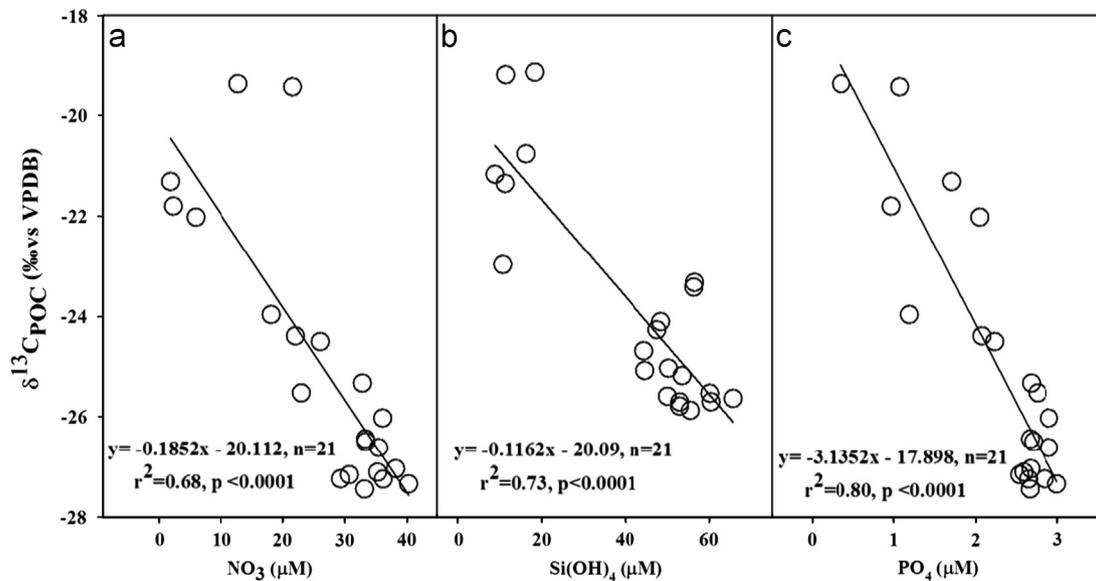
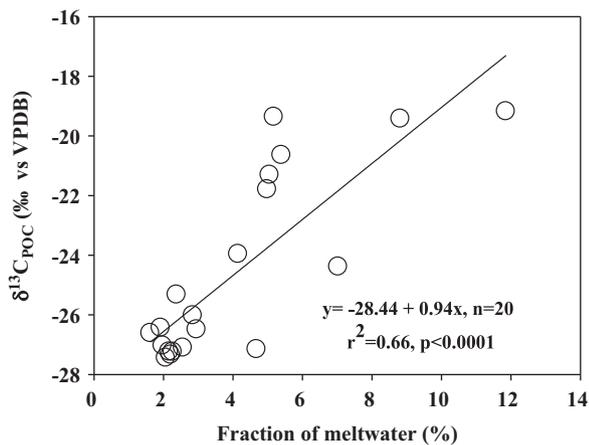


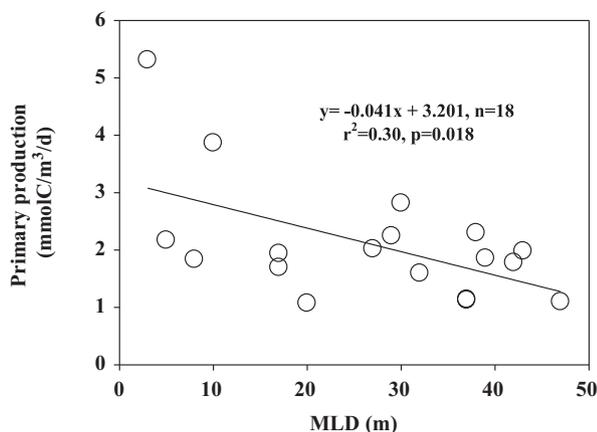
Fig. 4. Relationship between  $\delta^{13}\text{C}_{\text{POC}}$  and POC concentration in the upper 100 m in Prydz Bay. Different symbols represent samples collected from different depths. The relationship shown includes all data points.



**Fig. 5.** Relationship of surface  $\delta^{13}\text{C}_{\text{POC}}$  versus salinity-normalized macronutrient ((a)  $\text{NO}_3^-$ ; (b)  $\text{Si(OH)}_4$ ; (c)  $\text{PO}_4^{3-}$ ) concentrations in Prydz Bay. Salinity of 34.50 is chosen for normalization, as it was the mean salinity of the upper 100 m in Prydz Bay during the cruise.



**Fig. 6.** Relationship of surface  $\delta^{13}\text{C}_{\text{POC}}$  versus the fraction of meltwater ( $f_i$ ).



**Fig. 7.** Relationship of surface primary production ( $\text{mmolC/m}^3/\text{d}$ ) versus mixed layer depth (m) in Prydz Bay.

production is negatively correlated to MLD (Fig. 7), indicating that enhanced upper water column stratification regulates phytoplankton photosynthesis. This can be achieved because a shallower mixed layer holds phytoplankton closer to the surface where light

levels are higher, while light availability is a key determinant in phytoplankton production in the Southern Ocean (Mitchell et al., 1991; Sunda and Huntsman, 1997). Similar correlation has also been reported in the sea-ice zone west of the Antarctic Peninsula (Vernet et al., 2008). This is consistent with published results that the extent and duration of phytoplankton blooms during austral summers in the Antarctic waters largely depend on the continuing stability of the upper water column (Arrigo et al., 1999; Villinski et al., 2000). Changes in primary production control the degree of nutrient drawdown and air-sea  $\text{CO}_2$  disequilibrium that may occur. Interestingly, spatial coherence of POC concentration and density ( $\sigma_t$ ) field in the surface waters has been observed during the period of sea ice receding in the Ross Sea (Smith and Nelson, 1985). It is worth noting that the PP-MLD correlation is significant but not very strong ( $r^2=0.30$ ,  $p=0.018$ ), implying the complexity of controlling factors besides changes in MLD on the process of carbon fixation in the study area. The possible underestimation of PP (exclusion of urea uptake,  $\sim 10\%$ ) may also cause some uncertainty to the PP-MLD correlation.

It should be noted that under the lowered ambient  $\text{CO}_2(\text{aq})$  availability, it is probable that the Southern Ocean phytoplankton (mainly diatoms and *Phaeocystis*) may also take  $\text{HCO}_3^-$  (which is isotopically 'heavier' relative to  $\text{CO}_2$ ; Deines et al., 1974; Mook et al., 1974) as an inorganic carbon source (Tortell et al., 2008), likely making the product POC more enriched in  $^{13}\text{C}$  as well. However, to date no such studies have been reported in Prydz Bay and beyond the scope of this study, thus limiting us from evaluating the possible effect of inorganic carbon source on POC isotopic signature.

It is also noteworthy that ice melting may induce complex consequences besides enhanced water column vertical stability (like phytoplankton size/species composition, ice-derived organic matter release, iron release, etc.), which were also able to contribute to elevated  $\delta^{13}\text{C}_{\text{POC}}$  signatures (Arrigo et al., 1999; Gibson et al., 1999; Kocczynska et al., 1995; Munro et al., 2010; Trull and Armand, 2001). Gibson et al. (1999) have shown that sea-ice-hosted algae is very much enriched in  $^{13}\text{C}$  compared to the seawater suspended POM, and its contribution to the elevated sedimentary organic matter  $\delta^{13}\text{C}$  values is most prominent in early spring. The release of iron from sea ice may be in particular important for meltwater promoting production and elevating  $\delta^{13}\text{C}_{\text{POC}}$  values. Trull and Armand (2001) have demonstrated that

increased iron availability may preferentially promote large diatom growth (especially *F. kerguelensis*, which was the dominant species during our study), thus elevating upper water column  $\delta^{13}\text{C}_{\text{POC}}$  during an iron release experiment (SOIREE) in the Southern Ocean. Moreover, high concentrations of exopolymeric substances (EPS) have been observed in the Antarctic sea ice (Dumont et al., 2009; Meiners et al., 2004; Underwood et al., 2010). Secreted by sea ice algae and bacteria, the negatively charged EPS may bind selectively to dissolved iron and act as an organic ligand, thus increasing the bioavailability of iron (van der Merwe et al., 2009). It is probable that the  $\delta^{13}\text{C}_{\text{POC}}$  values may be indirectly impacted (elevated) due to the release of EPS. All these may partly explain the relatively weak correlation between  $\delta^{13}\text{C}_{\text{POC}}$  and MLD ( $\delta^{13}\text{C}_{\text{POC}} = -0.15 \times \text{MLD} - 20.9$ ,  $r^2 = 0.51$ ,  $p < 0.001$ ,  $n = 24$ ) observed here. It all further highlights that ice melting is a key physical driving force in regulating carbon isotope biogeochemistry in Antarctic waters. Interestingly, the correlation between  $\delta^{13}\text{C}_{\text{POC}}$  and  $f_i$  observed here suggests that although ice melting is a key factor in controlling  $\delta^{13}\text{C}_{\text{POC}}$  in the Antarctic waters, it may not be the only one. A recent study has suggested that submarine ground discharge (SGD) may be an important water source in the Antarctic marginal ice zone (Uemura et al., 2011), which may add to the uncertainty of our Ra-S tracer system. However, information about SGD in the Prydz Bay region is not available to further refine the Ra mass balance. Undoubtedly, more comprehensive studies are necessary to improve our understanding of mechanisms regulating  $\delta^{13}\text{C}_{\text{POC}}$  and its environmental implications in the scarcely studied Prydz Bay.

## 5. Conclusions

We report an evident N–S difference in surface water  $\delta^{13}\text{C}_{\text{POC}}$  in Prydz Bay, which is positively correlated to changes in the fraction of meltwater estimated from  $^{226}\text{Ra}$  isotope and salinity, implying that ice melting may have played a key role in affecting surface ocean carbon isotope biogeochemistry. We propose that this may be achieved because the input of freshwater by ice melting creates a more stable water column and thus creates a more favorable light environment, which promotes phytoplankton production. The subsequent biological drawdown of  $\text{CO}_2$  in surface waters will allow a decreased carbon isotope fractionation during carbon fixation, and making the product POC more enriched in  $^{13}\text{C}$ . This proposed physical–biological coupling is supported by the correlations of primary production and  $\delta^{13}\text{C}_{\text{POC}}$  to surface ocean mixed layer depth, POC and macronutrient concentrations. Interestingly, other possible factors (eg., release of iron and exopolymeric substances from sea ice, shifts in phytoplankton species composition) induced by ice melting cannot be simply excluded and may also have played a role in contributing to elevated  $\delta^{13}\text{C}_{\text{POC}}$  values. Our results highlight the importance of ice melting in regulating carbon isotope biogeochemistry in the Antarctic waters. Future study integrating surface ocean carbon dynamics with POC export flux and possibly the sediment record will further improve our knowledge on the carbon biogeochemical cycle in the polar oceans.

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