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ORIGINAL PAPER

Estimating stable carbon isotope values of microphytobenthos in the Arctic for application to food web studies

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Abstract Most studies on Arctic food webs have neglected microphytobenthos as a potential food source because we currently lack robust measurements of $\delta^{13}C$ values for microphytobenthos from this environment. As a result, the role of microphytobenthos in high latitude marine food webs is not well understood. We combined field measurements of the concentration of aqueous carbon dioxide and the stable carbon isotopic composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) from bottom water in the Beaufort and Chukchi seas with a set of stable carbon isotopic fractionation factors reflecting differences in algal taxonomy and physiology to estimate the stable carbon isotope composition of microphytobenthos-derived total organic carbon ($\delta^{13}C_p$). The $\delta^{13}C_p$ for *Phaeodactylum tricornutum*, a pennate diatom likely to be a dominant microphytobenthos taxon, was estimated to be -23.9 ± 0.4 ‰ as compared to a centric diatom (*Porosira glacialis*, $\delta^{13}C_p = -20.0 \pm 1.6$ ‰) and a marine haptophyte (*Emiliana huxleyi*, $\delta^{13}C_p = -22.7 \pm 0.5$ ‰) at a growth rate (μ) of 0.1 divisions per day (d^{-1}). $\delta^{13}C_p$ values increased by ~ 2.5 ‰ when μ increased from 0.1 to a maximum growth rate of 1.4 d^{-1}. We compared our estimates of $\delta^{13}C_p$ values for microphytobenthos with published measurements for other carbon sources in the Arctic and sub-Arctic. We found that microphytobenthos values overlapped with pelagic sources, yet differed from riverine and ice-derived carbon sources. These model results provide valuable insight into the range of possible isotopic values for microphytobenthos from this region, but we remain cautious in regard to the conclusiveness of these findings given the paucity of field measurements currently available for model validation.

Keywords Dissolved inorganic carbon (DIC) · Microphytobenthos · Stable carbon isotope fractionation · Beaufort Sea · Chukchi Sea

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Introduction

Projected impacts of climate change and industrial development on the marine environment necessitate an improved understanding of energy flow and food web structure in the Arctic (Carmack et al. 2006). Stable carbon isotope analyses of total organic carbon (TOC) from organisms can provide an effective tool to determine contributions from different primary production sources to Arctic food webs (Hobson et al. 2002; Budge et al. 2008; Dunton et al. 2012). Typically assessed primary producer sources in Arctic food web studies are pelagic, riverine, and sympagic organic

matter. These sources differ in their $\delta^{13}C$ values due to variation in the composition and availability of the carbon source used in photosynthesis. Pelagic phytoplankton obtain dissolved inorganic carbon (DIC) from surface ocean waters where the global mean stable carbon isotope composition ($\delta^{13}C_{DIC} = 1.5 \pm 0.8$ ‰) (Gruber et al. 1999) is enriched in ^{13}C relative to terrestrial sources such as atmospheric CO_2 ($\delta^{13}C_{atm} = -7.9$ ‰) (Farquhar et al. 1989). Riverine organic matter $\delta^{13}C$ values are low compared to marine sources because riverine organic matter consists largely of highly degraded terrestrial C_3 plants, including tundra taiga and angiosperms, that fix atmospheric CO_2 (Naidu et al. 1993; Goñi et al. 2000, 2005). Ice algae can have a unique stable carbon isotope composition relative to pelagic and riverine sources due to limited exchange of DIC in the brine channel matrix (e.g., Fischer 1991; Kennedy et al. 2002; Wang et al. 2014). At high levels of photosynthesis in a closed or semi-closed system, restricted exchange results in decreased expression of isotopic fractionation (Hobson et al. 1995; McMahon et al. 2006; Søreide et al. 2013).

Microphytobenthos is often not included as a potential source of primary production to Arctic food webs despite its prevalence on shallow shelves in the Arctic (Matheke and Horner 1974; Horner and Schrader 1982; Glud et al. 2009). Microphytobenthos is a distinct algal community dominated by pennate diatoms in the Arctic that develops exclusively on the sediment surface (Glud et al. 2009; Wulff et al. 2009 and references therein). Due to challenges associated with sample collection in the Arctic, including limited access to shallow stations on oceanographic field campaigns, the separation of microphytobenthos-derived organic matter from sediment samples and direct measurements of its isotopic composition are rare.

At lower latitudes, the isotopic composition of microphytobenthos is well characterized based on actual measurements (France 1995 and references therein). Techniques such as centrifugation in colloidal silica (Blanchard 1990), sediment scrapes of microphytobenthos colonies, collection of gut contents from known consumers of microphytobenthos, and additional methods reviewed by Oakes et al. (2005) have been used in temperate, tropical, and subtropical systems to isolate microphytobenthos for bulk and compound-specific stable isotope analysis (e.g., Oakes et al. 2005 and references therein; Evrard et al. 2010; Oakes et al. 2010a). However, robust measurements of the isotopic composition of microphytobenthos are difficult to perform due to the potential for contamination from additional organic matter sources such as microbial biomass, meiofauna, and detritus. To avoid the introduction of impurities associated with extant sampling techniques, innovative compound-specific predictive modeling approaches have been employed in order to constrain estimates for microphytobenthos $\delta^{13}C$ values (Evrard et al. 2010, 2012; Oakes et al. 2010b).

In the Arctic, predictive models are also especially useful because little is known about the spatial distribution of microphytobenthos, making sample collection difficult and, most always, opportunistic. To our knowledge, there are no published values of microphytobenthos stable isotope values from the Arctic Ocean (our study region). In a recent study, McTigue and Dunton (2014) were able to isolate microphytobenthos from Chukchi Sea sediments using a method developed by Blanchard (1990). However, they were unable to produce a reliable isotope measurement on the sample to include as an additional isotopic end member in their study.

Ideally, microphytobenthos sample analysis and predictive modeling approaches would be used in concert to produce a confident estimate of microphytobenthos isotopic composition. Combined results from actual measurements, predictive models for microphytobenthos, and isotopic labeling in lower latitude environments have provided insight into broad ecological questions regarding organic matter pathways and contributions of carbon sources to benthic consumers (e.g., Middelburg et al. 2000; Evrard et al. 2010; Van den Meersche et al. 2011). Microphytobenthos stable isotope research from studies conducted at lower latitudes provides direction for future research efforts in the Arctic and sub-Arctic.

We present an approach that estimates the stable carbon isotopic composition of microphytobenthos (TOC) from coastal regions of the Beaufort and Chukchi seas for future consideration in Arctic food web studies. The central objective of our study was to identify the bounds for estimates of $\delta^{13}C$ values of TOC derived from microphytobenthos, given variation in DIC composition and availability and algal taxonomy and physiology. First, we measured the concentrations and stable carbon isotopic compositions (expressed here as $\delta^{13}C$ values) of DIC in bottom water samples from the Beaufort shelf. We then used empirically derived quantitative relationships between the $\delta^{13}C$ values of DIC, the aqueous concentration of CO_2 ($[CO_2]aq$) in seawater, and a range of previously reported photosynthetic fractionation factors (ε_p) (Laws et al. 1995; Popp et al. 1998) that account for differences in algal taxonomy, morphology, and growth rate (μ) to constrain the $\delta^{13}C$ values of microphytobenthos TOC ($\delta^{13}C_p$) in this region. We compared these estimates to $\delta^{13}C$ values of previously measured carbon sources (i.e., pelagic, riverine, sympagic) in the Arctic and to $\delta^{13}C_p$ from lower latitudes.

Materials and methods

Sample collection and preparation

Seawater samples ($n = 18$) were collected from ~5 m above the sediment–water interface along four transects in the Beaufort and Chukchi seas in October 2012 during a research cruise on the USCGC Healy (HLY1203) (additional information available in Online Resource 1). Transects were located at the mouths of Barrow Canyon and the Mackenzie River, to the east of Point Barrow, and across Amundsen Strait (Fig. 1). Water depth ranged from 28 to 346 m. At each station sampled ($n = 18$), a CTD rosette (Seabird 911 plus system using dual temperature, conductivity, and oxygen sensors) was deployed to record conductivity, temperature, pressure, transmittance, and fluorescence measurements on downcasts (data are available in Online Resource 1) and to collect water samples in Niskin bottles linked to the CTD rosette. Samples for DIC isotope analyses were transferred from the Niskin bottles to 300-mL borosilicate bottles pre-cleaned with a 10 % solution of HCl without headspace or introduction of bubbles. Samples were immediately poisoned with 100 µL of mercuric chloride ($HgCl_2$) to suspend biological activity. Samples were then wrapped in Teflon tape, closed with a screw-on cap, and stored in the dark at room temperature (25 °C). Seawater samples were also taken from Niskin bottles for shipboard measurements of DIC concentration (poisoned as previously described), total alkalinity (TA), and nutrient analyses. Nutrient samples were stored frozen at −20 °C in plastic vials for subsequent analysis of nitrate, nitrite, phosphate, silicic acid, and ammonium.

Sample analysis

Nutrient samples were analyzed at the University of Alaska Fairbanks (UAF) using an Alpkem Flow Solution IV Autoanalyzer (OI Analytical, College Station, TX) (Whitledge et al. 1981). Analytical precision for triplicate nutrient measurements was between 0.03 and 0.05 µmol kg^{-1}. Commercially available certified standards (Ocean Scientific International and Wako Chemical), used for instrumental calibration, were included in the sample run as quality control. Shipboard measurements of DIC concentration (µmol kg^{-1}) were performed using a gas extraction/coulometric detection system that consisted of a VINDTA 3C (Versatile Instrument for the Detection of Total Alkalinity) (Marianda Co, Kiel, Germany) interfaced with a CO_2 coulometer (coulometer 5011, UIC Inc, USA). TA (µmol kg^{-1}) was measured by potentiometric titration with HCl (see Bates 2001 for details) using the same VINDTA system. Analytical precision was tracked using repeated measurements of Certified Reference Materials (CRMs, provided by A.G. Dickson, Scripps Institution of Oceanography) and was within 0.02 % (~0.4 µmol kg^{-1}).

Stable carbon isotope analyses of DIC samples were conducted at the Stable Isotope Laboratory at Oregon State University (OSU) following the methods of Torres et al. (2005). Seawater was transferred to Labco Exetainer Vials (7 mL), closed with rubber septa, and cooled to 13 °C in a water bath for 15 min. Samples were flushed with He

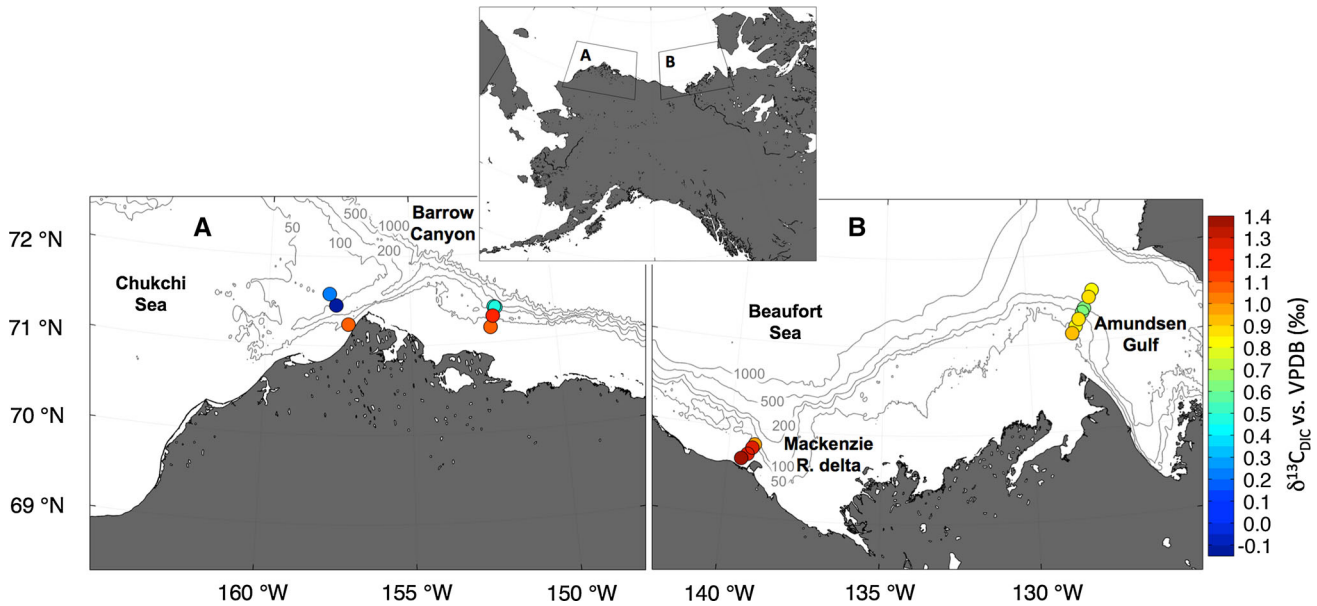

Fig. 1 $\delta^{13}C_{DIC}$ values (‰) measured from Beaufort Sea bottom water (~5 m from sediment–water interface) at sampling locations in the Beaufort and Chukchi seas for seawater collection and CTD casts

(Matheson UHP grade) for 5 min, then acidified with ~0.1 mL of 85 % orthophosphoric acid (EMD Chemicals HPLC grade). Samples were allowed to equilibrate for 10 h before stable carbon isotope analysis. DIC samples were analyzed using a Finnigan GasBench II interfaced with a Delta V Plus (Thermo Fisher Scientific, Bremen, Germany) continuous-flow isotope ratio mass spectrometer (CF-IRMS). Instrumental calibration was based on calcium carbonate (solid) international laboratory standards (NBS19 and NBS20). An internal laboratory standard (3 mM sodium bicarbonate in solution) that could be analyzed in the same way as the water samples was used for secondary calibration (Torres et al. 2005). Analytical precision was ±0.04 ‰, expressed as 1 standard deviation (SD) calculated from replicate ($n = 10$) analyses of aqueous 3 mM sodium bicarbonate (internal laboratory standard) performed throughout the sample run. Sample precision ($n = 3$, Station 48, expressed as 1 SD) was ±0.01 ‰. Sample reproducibility, calculated from replicate ($n = 11$) sample analyses was ±0.06 ‰ (expressed as 1 SD). Stable carbon isotope compositions of DIC are expressed using conventional delta (δ) notation in parts per thousand (‰) based on the following equation:

$$\delta X = \left[\left(R_{\text{sample}}/R_{\text{standard}}\right) - 1\right] \times 1000 \quad (1)$$

where $\delta X = \delta^{13}C$, R is the ratio of $^{13}C/^{12}C$ in seawater, and R_{standard} is that of the standard reference material Vienna Pee Dee Belemnite (VPDB).

Calculations

CO_2 concentration ($[CO_2]$aq, μmol kg^{-1}) was calculated using CO2SYS version 1.05. DIC, TA, temperature, salinity, phosphate, and silicate data were input using the thermodynamic model, dissociation constants, and solubility equations following Lewis and Wallace (1995).

Fractionation factors for C_3 photosynthesis (ε_p) were modeled using a suite of equations that describe the relationship between $[CO_2]$aq, algal growth rate μ (d^{-1}), and ε_p (Laws et al. 1995; Popp et al. 1998). Laws et al. (1995) expressed ε_p in terms of μ and $[CO_2]$aq, ($r^2 = 0.97$, $n = 5$) as follows:

$$\mu/[CO_2]\text{aq} = -0.015 \times \varepsilon_p + 0.371 \quad (2)$$

In a subsequent study, Popp et al. (1998) examined the influence of cell geometry on ε_p for a diverse group of algal taxa, all of which occur in the sub-Arctic and Arctic marine environments (Krebs 1983; Medlin et al. 1996; von Quillfeldt et al. 2003; Smyth et al. 2004): *Porosira glacialis* (centric diatom), *Emiliana huxleyi* (haptophyte), *and Phaeodactylum tricornutum* (pennate diatom). At $\mu > 0$, differences in algal morphology influence carbon ($[CO_2]$aq) supply and demand, resulting in species-specific ε_p (Popp et al. 1998). Empirically derived regression relationships have been determined to describe the term ε_p for a centric diatom (*P. glacialis*, $\varepsilon_p^a = 25.5 - 1118.2\ \mu/[CO_2]$aq, $\mu = 0.3$ d^{-1}, $r^2 = 0.75$, $n = 7$), a marine haptophyte (*E. huxleyi*, $\varepsilon_p^b = 24.6 - 137.9\ \mu/[CO_2]$aq, $\mu = 0.6$ d^{-1}, $r^2 = 0.87$, $n = 9$), and a pennate diatom (*P. tricornutum*, $\varepsilon_p^c = 25.5 - 52.6\ \mu/[CO_2]$aq, $\mu = 1.4$ d^{-1}, $r^2 = 0.78$, $n = 8$) (Popp et al. 1998). Superscripts a–c for species-specific ε_p correspond to $\delta^{13}C_p$ superscripts in Table 1.

We also calculated ε_p for the pennate diatom, *P. tricornutum* exposed to the range of $[CO_2]$aq and $\delta^{13}C_{DIC}$ observed at our field sites at three growth rates ($\mu = 0.1$ d^{-1}, $\mu = 0.4$ d^{-1}, $\mu = 1.4$ d^{-1}). We selected the pennate diatom as representative of microphytobenthos due to its relative dominance in polar microphytobenthos community assemblages. We investigated changes in ε_p over a range of typical growth rates given low levels of irradiance and cold temperatures in polar environments (Longhi et al. 2003; Karsten et al. 2006). Although growth rates for polar benthic diatoms are typically $\mu = 0.3$–0.5 d^{-1}, growth rates as high as $\mu = 1.24$ d^{-1} have been observed (Longhi et al. 2003; Karsten et al. 2006). We selected $\mu = 1.4$ d^{-1} as the upper limit for algal growth rate following Laws et al. (1995) because μ rarely exceeds two doublings per day in the natural environment (Laws et al. 1987). Additionally, the maximum algal growth rate observed in the Arctic during a highly productive under-ice phytoplankton bloom was 1.44 d^{-1} in the Chukchi Sea (Arrigo et al. 2012). This value is likely the absolute maximum growth rate (and may be an overestimate of ambient rates of growth) given strong light attenuation at depth and high sediment loading on the Beaufort shelf.

Fractionation factors (ε_p) can then be used to determine the stable carbon isotope composition of bulk algal biomass ($\delta^{13}C_p$), following the theoretical relationship between the stable isotopic compositions of the carbon source ($\delta^{13}C_{DIC}$) and product ($\delta^{13}C_p$) for photosynthesis:

$$\varepsilon_p = 1000 \times (\delta^{13}C_{DIC} - \delta^{13}C_p)/(1000 + \delta^{13}C_p) \quad (3)$$

Significant differences between $\delta^{13}C_p$ values estimated for *P. tricornutum* at low ($\mu = 0.1$ d^{-1}), intermediate ($\mu = 0.4$ d^{-1}), and maximum ($\mu = 1.4$ d^{-1}) growth rates were identified using a one-way analysis of variance (ANOVA) with growth rate as the factor in conjunction with Tukey's post hoc test which corrects for family-wise error rate.

Unfortunately, there are few concurrent measurements of more than two of the parameters ($\delta^{13}C_{DIC}$, $\delta^{13}C_p$, $[CO_2]$aq, and μ) needed to validate our model, even at lower latitudes. To provide support for our model results, we first calculated a "fractionation factor" derived from the difference between $\delta^{13}C_{DIC}$ and $\delta^{13}C_p$ values measured in a subtropical subtidal

Table 1 Estimates of ε_p and $\delta^{13}C_p$ values for microphytobenthos based on measured $\delta^{13}C_{DIC}$ values and calculations of $[CO_2]aq$ measured in bottom water in the Beaufort Sea

Station	Water depth (m)	$\delta^{13}C_{DIC}$	$[CO_2]aq$	ε_p^a $\mu = 0.1$ d^{-1}	$\delta^{13}C_p^a$	ε_p^b $\mu = 0.1$ d^{-1}	$\delta^{13}C_p^b$	ε_p^c $\mu = 0.1$ d^{-1}	$\delta^{13}C_p^c$	$\delta^{13}C_p^c$ $\mu = 0.4$ d^{-1}	$\delta^{13}C_p^c$ $\mu = 1.4$ d^{-1}
9	47	1.0	18	19.2	−17.8	23.8	−22.2	25.2	−23.6	−22.7	−20.3
14	112	−0.1	72	24.0	−23.5	24.4	−23.9	25.4	−24.9	−24.7	−20.1
17	66	0.2	43	22.9	−22.2	24.3	−23.5	25.4	−24.5	−24.2	−20.2
23	33	1.1	19	19.6	−18.1	23.9	−22.3	25.2	−23.5	−22.7	−20.1
26	55	1.2	17	19.1	−17.6	23.8	−22.1	25.2	−23.4	−22.6	−19.9
28	165	0.5	33	22.1	−21.2	24.2	−23.2	25.3	−24.3	−23.8	−21.3
48	134	0.5	23	20.7	−19.8	24.0	−23.0	25.3	−24.2	−23.5	−21.6
49	346	0.8	23	20.7	−19.5	24.0	−22.7	25.3	−23.9	−23.2	−19.7
50	284	0.9	27	21.4	−20.1	24.1	−22.7	25.3	−23.8	−23.3	−21.8
52	172	0.6	36	22.4	−21.3	24.2	−23.0	25.4	−24.1	−23.7	−23.0
53	132	0.6	42	22.8	−21.7	24.3	−23.1	25.4	−24.1	−23.8	−21.5
55	75	0.9	28	21.5	−20.2	24.1	−22.7	25.3	−23.8	−23.3	−24.0
57	60	0.8	30	21.8	−20.6	24.1	−22.8	25.3	−23.9	−23.4	−22.6
59	54	0.9	30	21.8	−20.4	24.1	−22.7	25.3	−23.8	−23.3	−21.4
68	50	1.0	27	21.3	−19.9	24.1	−22.6	25.3	−23.7	−23.2	−22.3
69	42	1.3	20	20.0	−18.3	23.9	−22.1	25.2	−23.4	−22.6	−22.3
70	35	1.3	20	20.0	−18.3	23.9	−22.1	25.2	−23.4	−22.6	−21.4
71	28	1.4	21	20.3	−18.5	24.0	−22.1	25.3	−23.3	−22.6	−21.1
Mean		0.8	30	21.2	−20.0	24.1	−22.7	25.3	−23.9	−23.3	−21.4
1 SD		0.4	13	1.4	1.6	0.2	0.5	0.1	0.4	0.6	1.2

[a] Centric diatom (*P. glacialis*)

[b] Haptophyte (*E. huxleyi*)

[c] Pennate diatom (*P. tricornutum*)

shallow environment (Oakes et al. 2012). As such, the "fractionation factor" ($\varepsilon_p = 18.2$ ‰) reflects growth conditions specific to microphytobenthos such as limited DIC exchange through the sediment–water interface and competition for DIC within microphytobenthos biofilms (Oakes et al. 2012). We then applied this "fractionation factor" in concert with porewater $\delta^{13}C_{DIC}$ data from our study region (Coffin et al. 2013) to our model to estimate a $\delta^{13}C_p$ value and compared it to those we calculated in this study (Table 1). We selected porewater $\delta^{13}C_{DIC}$ values ($\delta^{13}C_{DIC} = -6 \pm 4$ ‰, mean ± SD, $n = 11$) as the carbon source for microphytobenthos ($\delta^{13}C_p$) in this validation exercise because it is a more probable source of inorganic carbon to microphytobenthos than bottom water. Porewater $\delta^{13}C_{DIC}$ values were reported in a study conducted in close proximity to our study sites in Beaufort Sea during the same time of year (Coffin et al. 2013).

Results

$[CO_2]aq$ ranged from 17 to 72 µmol kg^{-1} and $\delta^{13}C_{DIC}$ values varied from −0.1 to 1.4 ‰ (0.8 ± 0.4, mean ± 1 SD) for samples of bottom water at our sampling locations in the Beaufort and Chukchi seas (Table 1, Online Resource 1). The lowest $[CO_2]aq$ were observed near the mouth of the Mackenzie River and corresponded to the highest $\delta^{13}C_{DIC}$ values (Stations 68–71, Fig. 1, Online Resource 1). The highest $[CO_2]aq$ was observed in Barrow Canyon and corresponded to the lowest $\delta^{13}C_{DIC}$ value (Station 14, Fig. 1, Online Resource 1). For sites at depths shallower than 200 m, there was an inverse correlation between $\delta^{13}C_{DIC}$ and depth ($r = -0.80$, $n = 14$). Samples from Barrow Canyon did not follow this depth gradient (Stations 14, 17, Online Resource 1).

Based on our field measurements of $[CO_2]aq$ and $\delta^{13}C_{DIC}$ and a low algal growth rate ($\mu = 0.1$ d^{-1}) modeled $\delta^{13}C_p$ values were highest for the centric diatom (*P. glacialis*, $\delta^{13}C_p^a = -20.0 \pm 1.6$ ‰), relative to those for the haptophyte (*E. huxleyi*, $\delta^{13}C_p^b = -22.7 \pm 0.5$ ‰), and the pennate diatom species (*P. tricornutum*, $\delta^{13}C_p^c = -23.9 \pm 0.4$ ‰) (Table 1; Fig. 2). For the pennate diatom (*P. tricornutum*), increasing the growth rate from low ($\mu = 0.1$ d^{-1}) and intermediate ($\mu = 0.4$ d^{-1}) levels to a maximum growth rate ($\mu = 1.4$ d^{-1}) resulted in significantly higher $\delta^{13}C_p$ values (one-way ANOVA, $F = 47.49$, $p < 0.0001$) (Table 1) with an increase of 2.5 ‰ over the growth range. Mean $\delta^{13}C_p$ at $\mu = 0.4$ d^{-1}

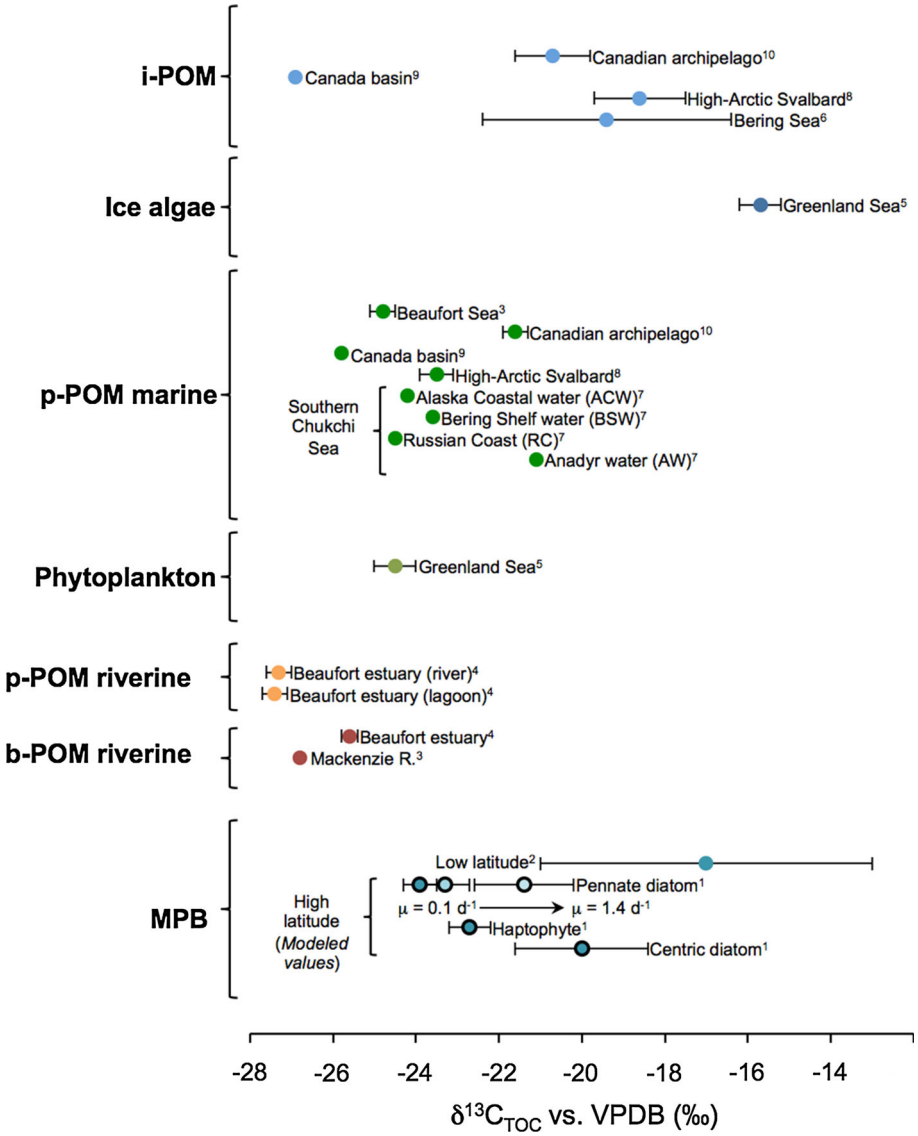

Fig. 2 $\delta^{13}C$ (‰) values for TOC (*circles*) from primary production sources in the Arctic, sub-Arctic, and low latitude marine environments (mean ± 1 SD). Symbols outlined in black are modeled values from the study. Particulate organic matter (POM) measured in ice (i-POM), water (p-POM), and sediment (b-POM) from the marine and riverine environment ([1]this study, [2]France 1995; [3]Naidu et al. 2000; [4]Dunton et al. 2012, [5]McMahon et al. 2006; [6]Wang et al. 2014; [7]Iken et al. 2010; [8]Søreide et al. 2013; [9] Iken et al. 2005; [10]Hobson and Welch 1992)

was not significantly different from those calculated at $\mu = 0.1\ d^{-1}$ ($p = 0.09$, Tukey's post hoc test).

The mean $\delta^{13}C_p$ value for the pennate diatom ($\delta^{13}C_p^c = -23.3 \pm 0.6$ ‰, $\mu = 0.4\ d^{-1}$), an algal taxon likely to be a dominant constituent of microphytobenthos, was more enriched in ^{13}C relative to previously reported values of riverine and estuarine TOC, including benthic-POM (b-POM) from river sediments and pelagic-POM from Arctic rivers and lagoons feeding into the Beaufort Sea (riverine p-POM) (Fig. 2). It was depleted in ^{13}C relative to ice algae and from sea ice particulate organic matter (i-POM). Although the mean $\delta^{13}C_p$ value for the pennate diatom was enriched in ^{13}C relative to marine p-POM from regions of low productivity such as the Canada Basin, it fell between reported ranges for most values for marine p-POM from the Beaufort and Chukchi seas and from neighboring regions in the Arctic (Fig. 2). Relative to reported values from studies conducted at lower latitude ($\delta^{13}C = -17 \pm 4$ ‰) (France 1995 and references therein), model estimates were depleted in ^{13}C.

When previously published data were applied to the model (see "Materials and methods" section for additional information on the model validation exercise), our model predicted a $\delta^{13}C_p$ value ($\delta^{13}C_p = -23.8$ ‰) that is consistent with those we report for the pennate diatom taxon ($\delta^{13}C_p^c = -23.9$ ‰) (Table 1).

Discussion

The primary aim of this study was to estimate the stable carbon isotopic composition of the microphytobenthic community in Arctic waters in order to assess their potential incorporation in stable isotope food web studies.

Microphytobenthos, a potential source of primary production to benthic food webs (Glud et al. 2009; Oakes et al. 2010a; Alderson et al. 2013), has rarely been considered in stable isotopic food web studies in the Arctic because it has not been described isotopically.

Stable isotopic analyses of microphytobenthos, and DIC from bottom water and porewater from high latitude environments, are necessary to determine whether our predictive model estimates are accurate. These isotopic measurements could serve as a validation to evaluate model behavior and adjust regression relationships used to model $\delta^{13}C_p$ values. Sample collection presents many challenges in the Arctic, given the nature of field sampling and the patchy distribution of microphytobenthos. Most oceanographic campaigns, including the one for this study, are carried out using research vessels in offshore waters. Marine coastal areas where microphytobenthos does occur are usually difficult to sample because of their shallow depth (e.g., Matheke and Horner 1974; Dunton et al. 2012). We were unable to collect microphytobenthos samples in concert with our bottom water DIC samples at study sites in the Beaufort and Chukchi seas due to these logistical constraints.

In the absence of comparative data from the Arctic or from microphytobenthos culture studies, our predictive modeling approach relies on several assumptions that cannot be fully corroborated at present. Empirical relationships from our model were developed from data for pelagic phytoplankton (suspended cells) (Laws et al. 1995; Popp et al. 1998), so we remain cautious in regard to conclusions from our findings. Although it is widely accepted that $\delta^{13}C$ values for benthic algae from marine coastal areas are, on average, more enriched than pelagic algae (France 1995), differences in $\delta^{13}C$ values of local DIC, availability of an inorganic carbon source ($[CO_2]aq$), algal growth rate, and microphytobenthos composition produce microphytobenthos values that deviate from this trend, as is evidenced by the range observed in more recent studies (Oakes et al. 2010a, b; Evrard et al. 2012). A potential difference between phytoplankton and microphytobenthos that could influence the fractionation factor (ε_p) and result in different $\delta^{13}C_p$ for phytoplankton and microphytobenthos is variation in growth rate. There is evidence to suggest, however, that phytoplankton growth rates are the same as, if not higher than, those for microphytobenthos growing in polar regions, where cold temperatures, low nutrient availability, and light limitations depress algal growth (Kirst and Wiencke 1995). The maximum growth rate used by Laws et al. (1995) and by this study ($\mu = 1.4\ d^{-1}$) was substantially higher than the maximum growth rate observed for polar microphytobenthos ($\mu = 1.24\ d^{-1}$) (Longhi et al. 2003; Karsten et al. 2006).

Stable isotopic variation between pelagic and benthic microalgae has also been attributed to differences in DIC availability and composition (Hecky and Hesslein 1995; France 1995). We might expect microphytobenthos to be isotopically distinct from pelagic sources given distinct benthic conditions such as DIC limitation in the benthic boundary layer at the seafloor (France 1995; Hecky and Hesslein 1995). Our use of $\delta^{13}C_{DIC}$ values from bottom water to constrain estimates for $\delta^{13}C_p$ could bias modeled values if porewater and bottom water DIC pools are isotopically distinct. However, recent evidence from our study region along the Alaskan shelf of the Beaufort Sea suggests that porewater DIC is not isotopically distinct from our bottom water measurements (Table 1) (Coffin et al. 2013). Porewater $\delta^{13}C_{DIC}$ measurements were made during the same time of year as our bottom water sample collection for isotopic analysis (Coffin et al. 2013). In all locations, porewater $\delta^{13}C_{DIC}$ values near the sediment water interface, where microphytobenthos would be growing, were very similar to that of typical seawater values (Coffin et al. 2013). Moreover, the range of $\delta^{13}C_{DIC}$ values reported for porewater from varying sediment depths ($\delta^{13}C_{DIC} = -6 \pm 4$ ‰, mean ± SD, $n = 11$) was the same as, or more depleted than, our DIC values from bottom water. This gives us confidence that our measured $\delta^{13}C_{DIC}$ values are appropriate to constrain estimates for microphytobenthos biomass. Additional porewater and bottom water sampling in the Arctic would bolster our estimates and elucidate a poorly studied compartment of the benthic carbon cycle.

Given the necessary assumptions for our modeling approach, our experimental results are a first step toward assessing the potential incorporation of microphytobenthos into marine Arctic food web studies with the hope that additional studies will refine this approach. Although we report some variability in $\delta^{13}C_{DIC}$ values and $[CO_2]aq$ across our study region, the ranges have little influence (~ 1.6 ‰) on modeled $\delta^{13}C_p$ values for the dominant algal constituent of microphytobenthos (pennate diatoms) (Horner and Schrader 1982) (Table 1).

Mean $\delta^{13}C$ values for microphytobenthos from lower latitude marine coastal sites (France 1995) were, on average, enriched in ^{13}C relative to those we report here. In the subtropics, there is considerable variation in microphytobenthos $\delta^{13}C_p$ values from photic sediments, from highly enriched values ($\delta^{13}C_p = -14.3 \pm 0.6$ ‰) (Oakes and Eyre 2014) to values more depleted than those we determine here ($\delta^{13}C_p = -25.5 \pm 1.0$ ‰) (Oakes et al. 2010a). In some cases, it is not possible to resolve benthic (microphytobenthos) production in lower latitude systems due to the presence of algal taxa in the microphytobenthos assemblage (e.g., cyanobacteria and green algae), which resemble other sources (e.g., pelagic suspended particulate

matter) (Evrard et al. 2012). Whereas isotopic measurements of microphytobenthos from lower latitude ecosystems integrate $\delta^{13}C_p$ values from multiple algal taxa (and from potential contaminants), our model describes variation in $\delta^{13}C_p$ values for individual algal taxa.

Low variability in our $\delta^{13}C_p$ estimates for individual microphytobenthos taxa also reflects the narrow range of $\delta^{13}C_{DIC}$ values we observed from bottom water from this region. $\delta^{13}C_{DIC}$ values have been described for surface waters in the world ocean as part of the Geochemical Ocean Sections (GEOSECS) program (Gruber et al. 1999) and, more recently, at varying depths in the Arctic Ocean (Griffith et al. 2012). Global measurements of $\delta^{13}C_{DIC}$ values, which are very consistent across regions ($\delta^{13}C_{DIC} = 1.5 \pm 0.8$ ‰), were slightly enriched compared to those observed in our study ($\delta^{13}C_{DIC} = 0.8 \pm 0.4$ ‰). Griffith et al. (2012) reported a range of $\delta^{13}C_{DIC}$ values (0.13–1.63 ‰) from offshelf sites in the Canada Basin that are in agreement with those we observed. In addition to expanding spatial coverage for $\delta^{13}C_{DIC}$ measurements at depth in the Arctic, our measurements narrow the sampling gap between surface waters and porewater (Coffin et al. 2013).

DIC measurements from this study revealed statistically significant depth-dependent gradients in $[CO_2]aq$ and $\delta^{13}C_{DIC}$ values wherein deeper sites contained higher $[CO_2]aq$ and depleted $\delta^{13}C_{DIC}$ values relative to shallower sites (Table 1; Fig. 1). An exception to this pattern was the Barrow Canyon transect, which is hydrographically and biologically distinct from the other Beaufort shelf sites (Pickart et al. 2009). Variation in $\delta^{13}C_{DIC}$ values can be explained by processes involving preferential uptake of the light stable isotope of carbon (^{12}C) (e.g., biological production) and those that release it into the DIC pool (e.g., carbon remineralization) (Holmden et al. 1998; Gruber et al. 1999) and by contributions from isotopically distinct sources such as riverine DIC (Macdonald et al. 2004). In the marine environment, biological production and carbon remineralization occur largely in surface waters and at the seafloor, respectively, creating a depth-dependent gradient in $\delta^{13}C_{DIC}$ values (Emerson and Hedges 2008).

$\delta^{13}C_{DIC}$ values can also be a useful indicator of DIC source given observed differences in $\delta^{13}C_{DIC}$ values from riverine and marine sources (Patterson and Walter 1994). To this end, one might have expected the Mackenzie River delta transect, where riverine organic material enters the Arctic Ocean (Macdonald et al. 2004) to have the lowest $\delta^{13}C_{DIC}$ values. Contrary to this expectation, $\delta^{13}C_{DIC}$ values at the Mackenzie River delta were most isotopically enriched in ^{13}C relative to other sampling locations. These relatively high $\delta^{13}C_{DIC}$ values corresponded to the lowest $[CO_2]aq$, possibly indicating that elevated benthic primary production resulted in subsequent depletion of $[CO_2]aq$ and drawdown of isotopically light DIC.

Elevated benthic primary production (growth rate) can also influence $\delta^{13}C$ values of microphytobenthos and is often mediated by environmental conditions, such as light, temperature, and nutrient availability (Fry and Wainright 1991; Kirst and Wiencke 1995; Korb et al. 1996; Pancost et al. 1997). Based on light limitation at depth and the maximum depth for microphytobenthos growth previously reported (Cahoon et al. 1990; Cahoon 1999; McGee et al. 2008), we would expect the contribution of microphytobenthos to be greatest at shallow sites (e.g., Stations 23, 79, 71) and at coastal locations that we were unable to access in the field. Palmer et al. (2013) measured 0.1 % light depth (euphotic depth) to be 37 ± 18 m in the Beaufort and Chukchi seas during the months of June and July under open water and under sea ice. This gives us confidence that considerable microphytobenthos growth could occur at stations <100 m (Online Resource 1, $n = 11$) and across much of the Chukchi and Beaufort seas due to their wide, shallow shelves. However, we do not expect microphytobenthos growth at stations >100 m depth (Online Resource 1, $n = 6$) where low light availability would limit photosynthesis.

We determined that within a selected growth range, $\delta^{13}C_p$ values for the dominant algal constituent of microphytobenthos (pennate diatoms) increased on the order of approximately 2.5 ‰. This indicates that isotopic values for microphytobenthos may vary seasonally but within a relatively small range (Fig. 2). Seasonal variability in $\delta^{13}C_p$ values may be pronounced, however, if algal community succession occurs in the benthos as in the pelagic realm during the course of the growing season (Moran et al. 2012) because individual taxa had distinct modeled values (Table 1; Fig. 2). Differences in the isotope values of algal taxa may be the result of varying expression of carbon concentrating mechanisms (CCMs), which have been observed in marine algae (mainly diatoms) (Giordano et al. 2005; Haimovich-Dayan et al. 2013). C_3 photosynthesis, as modeled here, is considered the predominant biochemical pathway for production in marine algae (Haimovich-Dayan et al. 2013 and references therein). However, biophysical and biochemical CCMs could result in variable fractionation factors and isotopically enriched algal organic matter relative to that of its inorganic carbon source.

Additionally, differences in fractionation in distinct algal taxa may result from variation in RuBisCO, the carbon dioxide fixation enzyme. Algal taxa use at least four known forms of RuBisCO (Ishida and Green 2002). Boller et al. (2011) measured isotopic discrimination at the enzyme level of a form of RuBisCO from *E. huxleyi*. This form of RuBisCO is also the dominant form in diatoms, rhodophytes, and certain dinoflagellate species (Ishida and Green 2002). It was characterized by low isotopic discrimination ($\varepsilon = 11.1$ ‰) relative to previously published values for additional enzymatic forms ($\varepsilon = 18$–29 ‰)

(Boller et al. 2011 and references therein) and relative to whole cell fractionation factors we report based on our field measurements ($\varepsilon = 21.2$–25.3 ‰, Table 1).

In summary, we provide model estimates of the $\delta^{13}C$ values of TOC originating from microphytobenthos in the Arctic. We also report a narrow distribution of $\delta^{13}C$ values of DIC and provide measurements of $[CO_2]aq$ from bottom water across the Beaufort and Chukchi seas during the onset of winter. Based on published $\delta^{13}C$ values of TOC from other sources of primary production in the Arctic and sub-Arctic, we suggest that $\delta^{13}C$ values of microphytobenthos may be distinct from those of riverine and sympagic origins, and from marine p-POM under conditions of low productivity. However, the stable carbon isotope composition of microphytobenthos was indistinguishable from that of marine p-POM under conditions of high productivity. Compared to previously reported microphytobenthos $\delta^{13}C$ values from studies outside of the Arctic, microphytobenthos values predicted by our model were depleted in ^{13}C. Further sample collection and analysis of microphytobenthos in the Arctic and sub-Arctic in combination with data from culture studies are of critical importance to investigate these differences and to improve this predictive model.

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Compliance with ethical standards

Conflicts of interest The authors have no conflicts of interest to declare.

Research involving human participants and/or animals This article does not contain any studies with human participants or animals performed by any of the authors.

Informed consent Informed consent was obtained from all individual participants included in the study.

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