Sources and Cycling of Particulate Organic Matter in Baffin Bay: A Multi-Isotope $\delta^{13}$C, $\delta^{15}$N, and $\Delta^{14}$C Approach

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The Canadian Arctic is warming three times faster than the rest of the planet. The impact of climate change on the Arctic carbon cycle, and in particular for Baffin Bay, remains poorly constrained. Sinking particulate organic matter (POMsink) is a key component of the biological carbon pump and provides a direct linkage between surface productivity and the preservation of carbon in marine sediments. While POMsink provides a rapid POM shunt to the deep ocean (days) the majority of marine POM is suspended (POMsusp) persists for years in the water column. Stable carbon ($\delta^{13}$C), nitrogen ($\delta^{15}$N) and radiocarbon ($\Delta^{14}$C) measurements are powerful tools for evaluating sources and cycling of POM. In this study, we measure depth-integrated (0-400m) POMsusp stable carbon ($\delta^{13}$C), nitrogen ($\delta^{15}$N) and radiocarbon ($\Delta^{14}$C) values at 11 stations in Baffin Bay. We use POM C:Na ratios to evaluate its diagenetic state. POMsusp $\delta^{13}$C and $\delta^{15}$N values ranged from $-21.6$‰ to $-29.5$‰, and $+3.84$‰ to $+7.21$‰, respectively. POMsusp $\Delta^{14}$C values ranged from $-41.8$‰ to $+76.8$‰. Together, our results suggest Baffin Bay POMsusp has multiple carbon and nitrogen sources. POMsusp $\delta^{13}$C and $\Delta^{14}$C are strongly correlated to surface salinity, indicating surface water has a strong influence on POMsusp isotopic composition and $\Delta^{14}$C-age. POMsusp from coastal Greenland stations have similar $\Delta^{14}$C values to surface dissolved inorganic carbon (DIC) and POM concentrations, consistent with primary production as the predominant POMsusp source in Eastern Baffin Bay. Positive POMsusp $\Delta^{14}$C values in central Baffin Bay suggest an accumulation of atmospheric “bomb” $^{14}$C in the sub-polar gyre. POMsusp exiting Davis Strait via the Baffin Island Current was determined to have a significant degraded, resuspended sediment component. Finally, POMsusp $\delta^{15}$N values highlight two distinct N sources in Baffin Bay: Pacific and Arctic nutrients at Northern gateway stations vs. the influx of Atlantic nutrients via Davis Strait along coastal Greenland. Overall, these first Baffin Bay POMsusp $\Delta^{14}$C values provide useful baseline data for rapidly changing Arctic ecosystem.

Keywords: particulate organic matter, radiocarbon, $^{12}$C, $^{15}$N, $^{14}$C, Baffin Bay, Arctic, C:N
INTRODUCTION

Particulate organic matter (POM) is one of the most important and biologically active reservoirs of carbon and nitrogen in the oceans. Whereas the POM pool (30 ± 5 GtC, ~2.3 GtN) is smaller than that of dissolved organic matter (~662 GtC, 32-77 GtN) and dissolved inorganic carbon (DIC; 38,000 GtC), marine POM cycles rapidly (Hansell et al., 2009; Sarmiento, 2013; Walker et al., 2016; Beaufre, 2019). POM is operationally defined as all organic matter retained by a 0.1μm filter. However, studies typically employ 2.0μm quartz or 0.7μm glass filters as they can be combusted prior to collection. POM therefore includes all living marine organisms larger than a bacterial cell, but approximately 90% of POM is non-living detritus (Cauwet, et al., 2016; Beaupre, 2016). POM is produced by primary producers via photosynthetic carbon fixation in the euphotic zone. The re-packaging of phytoplankton through zooplankton heterotrophy results in rapid export of sinking POM (POMsink) to the seafloor. Commonly known as the “biological carbon pump” (BCP), POMsink is exported to the sediments at rates of 2.8-5.7 GtC yr⁻¹ (Buesseler et al., 2020). However, only a small portion of POMsink reaches the sediment as most is remineralized to CO₂ or transformed to dissolved organic matter (DOM) via heterotrophic microbes prior to burial (Smith et al., 1992; Denman et al., 2007). Approximately ~90% of recently deposited POM in sediments is remineralized at the sediment/water interface. Nevertheless, POM burial at rates of 0.2 to 0.4 GtC yr⁻¹ allows for the long-term sequestration of atmospheric CO₂ (Passow and Carlson, 2012; Middelburg, 2019). The efficiency of the BCP varies with the availability of light, nutrients, sea surface temperature (SST), resident phytoplankton and zooplankton communities and polar sea-ice conditions (Honjo et al., 2010). Most BCP studies have focused on POMsink as the main carbon burial vector. However, recent work suggests small phytoplankton cells found in the suspended POM pool (POMsusp) are important contributors to the BCP (Richardson and Jackson, 2007; Close et al., 2013).

Stable carbon (δ¹³C) and nitrogen (δ¹⁵N) isotope measurements are useful tools for understanding organic matter sources and cycling. Whereas historical POM cycling studies relied on time-intensive and laborious deployment of sediment traps and mooring time-series, isotopic measurements provide detailed evidence for physical/biological processes and controlling POM cycling rates without the inherent need for long-term deployments and repeat study. It should be noted that long-term deployments provide information about temporal evolution, while CTD cast sampling reflects a short temporal window “snap shot” of POM cycling. POM δ¹³C and δ¹⁵N inform us of organic matter sources (e.g., terrestrial vs. marine) as well as biological processes (autotrophy vs. heterotrophy), with isotopic ratios being controlled by mass-dependent fractionation via carbon and nitrogen fixation pathways, trophic level enrichment, and nutrient sources (Descolas-Gros and Fontugne, 1990; Rau et al., 1992; Williams et al., 1992; Sigman and Casciotti, 2001; Fawcett et al., 2011). Marine phytoplankton δ¹³C and δ¹⁵N show a wide range of values (from −35‰ to −15‰ and +1‰ to +10‰, respectively). POM δ¹³C values in temperate waters typically range between −18‰ and −22‰, but more negative values are observed in polar regions as a result of temperature-dependent fractionation (Rau et al., 1982; Goericke and Fry, 1994).

In Baffin Bay, possible POMsusp δ¹³C sources include: i) slow-growing marine phytoplankton in colder, fresher waters (~27 to −30‰; Brown et al., 2014), ii) fast-growing phytoplankton in warmer, fresher waters affected by glacial meltwater (~21.8 to −24‰; Limoges et al., 2020) iii) canonical marine plankton values for this region (~24 to −26‰; Goericke and Fry, 1994), iv) sea-ice algae (~20 to −17‰; Tamelander et al., 2006; Roy et al., 2015; De La Vega et al., 2019), v) glacial run-off POM (~28.5‰; Holding et al., 2017) and vi) terrestrial plants (mosses, lichen, grasses; −28 to −20‰; Lee et al., 2009). POMsusp δ¹⁵N values are typically associated with nutrient sources (nitrate) fueling primary production, or the predominant mode of autotrophic or heterotrophic metabolism. For example, nitrate δ¹⁵N (δ¹⁵NO₃⁻) in the surface ocean has a large range (+2 to +20‰; Rafter et al., 2019), and is largely determined by nutrient availability and biological processes fractionating the surface nitrate pool (e.g., assimilation vs. denitrification and remineralization). Probable δ¹⁵NO₃⁻ signatures that can be incorporated into surface POM δ¹⁵N in Baffin Bay include nitrate from: the Atlantic Ocean (+4 to +6‰; Sherwood et al., 2021), the Pacific Ocean via the CAA (+7 to +8‰; Brown et al., 2015; Granger et al., 2018), and the Arctic Ocean (+5 to +7‰; Fripiat et al., 2018; Rafter et al., 2019).

Radioactivity (Δ¹⁴C) measurements serve as both a carbon source indicator (e.g. fossil vs. modern vs. atmospheric “bomb” carbon) and as a geochronometer (via radioactive decay). In addition to naturally produced ¹⁴C in the atmosphere, above-ground thermonuclear weapons testing in 1960s resulted in an atmospheric “bomb peak” that has allowed Δ¹⁴C to be used as a modern tracer of atmospheric carbon on short timescales. Previous studies have used POM Δ¹⁴C and stable isotope measurements of POM to evaluate POM cycling rates, and relative contributions of allochthonous vs. autochthonous detrital materials in a variety of systems. A study of size-fractionated POMsusp Δ¹⁴C from the California Current upwelling system showed that while most POMsusp is comprised of recently fixed photosynthetic material, the presence of negative POMsusp Δ¹⁴C values suggested contributions of pre-aged, re-suspended sediments to POMsusp in coastal systems (Walker et al., 2014). Hwang and co-workers (2010) used POMsink Δ¹⁴C and δ¹⁵N values to estimate the global contribution of pre-aged, continental margin material to open ocean POM.

POM is also a complex geochemical mixture. Compound class separations of total lipid extracts (TLE), acid soluble (AS) and acid-insoluble (AI) fractions suggest POM comprises materials with heterogeneous ¹⁴C-ages and chemical composition. Here TLE- and AI-POM are “pre-aged” and molecularly uncharacterized material, whereas AS-POM appears to be rich in biomolecules and has a Δ¹⁴C signature similar to surface DIC throughout the water column (Hwang and Druffel, 2003;
Hwang and Druffel, 2006; Roland et al., 2008). Previous work has also demonstrated a clear compositional and $^{14}$C-age difference between large vs. small POM size fractions. Whereas POM$_{\text{sink}}$ and large POM size-fractions (dominated by large autotrophs) are biochemically “fresh” and have younger $^{12}$C-ages, most evidence suggests POM$_{\text{susp}}$ and small POM size-fractions (dominated by re-suspended sediments and microbial cells) are “degraded” and have older $^{14}$C-ages (Walker et al., 2014; Benner and Amon, 2015; Walker et al., 2016). Whereas POM$_{\text{susp}}$ can appear $^{14}$C-modern and chemically “fresh” if derived from recent plankton blooms (e.g., Walker et al., 2014), coastal POM$_{\text{susp}}$ is also considered a source of $^{14}$C-depleted OM to the open ocean (Bauer and Druffel, 1998; Hwang et al., 2006; Roland et al., 2008).

Declining sea-ice cover and a prolonged “open water” season may cause considerable increases in primary production across the Arctic, with consequences for POM cycling (Arrigo and Dijken, 2015). Previous POM studies in Baffin Bay have focused on deployment of sediment traps to estimate export production and POM flux in the high-productivity North Water Polynya. These studies suggest high rates of POM export in Norther Baffin bay (5.9 g C m$^{-2}$ yr$^{-1}$) and seasonal variance in POM export. Most POM export occurs in the Spring and some retention of POM in the upper water column (100m) has been observed in late summer (Caron et al., 2004; Lalande et al., 2009). However, these flux estimates do not provide us with an understanding of the biological lability or geochemical impact of POM exported to deep Baffin Bay. There is a paucity of Arctic POM isotopic data and, to the best of our knowledge, no POM $\Delta^{14}$C data exist for Baffin Bay. Here we use the first POM$_{\text{susp}}$ $\Delta^{14}$C values with contemporaneous C,N, $\delta^{13}$C and $\delta^{15}$N values to evaluate POM sources and cycling in Baffin Bay.

METHODS

Baffin Bay Hydrographic Setting

Here we briefly describe the surface currents present in Baffin Bay and origin of surface waters sampled during the study (Figure 1). Baffin Bay is a large marginal sea lying between Kalaalit Nunaat (Greenland) and Qikiqtaaluk (Baffin Island), connected by straits to the Arctic Ocean and the Atlantic Ocean. Baffin Bay is characterized by dynamic surface currents environment, with a stark contrast in oceanographic conditions (e.g., SST, salinity, fluorescence, and nutrients) in Western vs. Eastern Baffin Bay (Figures 2A, B, S1–4). The Baffin Island Current (BIC) flows southward along the Baffin Island shelf and slope before exiting Davis Strait into the Labrador Sea. The BIC is composed of cool, fresh Arctic Water (AW) from recent sea-ice melt from the Arctic Ocean and Canadian Arctic Archipelago (CAA) which enters Baffin Bay via several northern gateways (NG) – Nares Strait, Jones Strait, and Lancaster Sound. In Eastern Baffin Bay, relatively warm and salty waters enter from the North Atlantic, forming the West Greenland Current (WGC), and flow north along the Greenland shelf. The WGC is a continuation of the East Greenland Current (EGC), composed of Arctic waters flowing southwards along the eastern coast of Greenland, with contributions from the warm and saline Irminger Current in the North Atlantic (Hamilton and Wu, 2013). As the WGC progresses northward, it becomes fresher and cooler, due to mixing with glacial meltwater and mixing with central Baffin Bay water (Münchow et al., 2015). The WGC terminates near Smith Sound (75°N-77°N), before joining Arctic Water outflows from the CAA to form the BIC (Melling et al., 2001; Tang et al., 2004). Together, the northwards-flowing WGC and southwards-flowing BIC form a cyclonic circulation pattern and sub-polar gyre in Baffin Bay. The eastern side of Baffin Bay also receives more meteoric

![FIGURE 1](https://www.frontiersin.org/static_html/KH6847-2022-00077/v7/F1.png)
freshwater input from melting of the Greenland ice sheet (Hamilton and Wu, 2013). This difference in East vs. West surface water properties results in differences in phytoplankton communities, sea ice conditions and rates of primary production in the region. For example, the timing and intensity of phytoplankton blooms is different on the Eastern vs. Western side of Baffin Bay and can clearly be seen in fluorescence values of the deep chlorophyll-a maximum (DCM; Figure 2C). The depth of the DCM in our sample stations ranged from 13 to 44 metres, with an average of depth of 32 ± 10 metres (n=11; Figure S3). Annual POM flux is generally higher on the eastern side of northern Baffin Bay relative to the western side (Lalande et al., 2009). It is important to note that Baffin Bay is a marginal sea ice zone. The region experiences full sea-ice coverage from December to April. Due to the relatively warm West Greenland Current, ice cover decreases earlier along the Greenland coast than on the western side of Baffin Bay (Tang et al., 2004). By late summer, Baffin Bay is typically clear of extensive sea-ice, although icebergs are common, especially in proximity to fjords.

**Sampling Collection and Preparation**

POM susp samples were collected from 11 stations in July 2019 aboard the CCGS Amundsen (Figure 2A). A main goal of this broader study was to sample depth profiles for isotopic characterization of dissolved organic carbon. Due to a restricted water budget, low expected POM concentrations, collected POM susp samples comprise depth integrated filtrations of seawater from 0 to 400m depth, filtered directly from 12L Niskin bottles. POM susp was filtered either by gravity and/or by a peristaltic pump using acid cleaned (10% HCl) silicone tubing onto pre-combusted (540°C/2h) 70mm quartz fiber filters (Whatman QMA; 2.0μm) held in a custom stainless-steel manifold. Samples comprise seawater POM from 15 to 20 discrete Niskin bottles, depending on the depth of the station. Between 60±10 mL and 1.50±0.12 L of seawater from each Niskin was passed through the filter. Larger seawater volumes (>1 liter) were sampled at depths of 0m, 20m, 50m, 100m, 200m, 300m, and 400m. Between 4.9±0.2 L and 12.2±0.3 L were passed through filters in total, with most stations having ~7.1 liters in total. After sample collection, POM susp QMA filters were placed in pre-combusted (540°C/2h) aluminum foil envelopes, frozen immediately and stored at -20°C until sample processing at the University of Ottawa. Measurements of SST, salinity, and fluorescence were taken via the CTD rosette instrument package equipped with 24, 12L Niskin bottles including a Seabird SBE911plus CTD profiler and ECO-Fl Chlorophyll-a fluorometer for 53 stations in Baffin Bay (Figures 2A–C).
In the lab, filters were oven dried overnight (50°C/8h) and vapor-phase acidified at ambient pressure in a clean glass desiccator bell with 5 mL of 12N HCl for 4 hours to remove particulate inorganic carbon (PIC). To avoid the use of hydrocarbon-containing grease, the desiccator bell was sealed with ~1mL 85% phosphoric acid placed on its stoneground glass joint. POM filters were subsampled by cutting approximately one-third of the filter. A time of 4 hours was used instead of common 12h or “overnight” acidification methods based on lab tests showing complete removal of 10 mg of NaHCO₃ on filters under similar conditions in less than 2 hours (S. Beaupré and B. Walker, unpublished data). Our filters contain far less than 10 mg of total mass, and substantially less inorganic carbon. After acidification, sample filters were again oven dried (50°C overnight) to remove HCl and H₂O vapor and stored in a low humidity, desiccator cabinet until further processing for isotopic analysis.

**POM悬浮 Concentrations, Stable Isotope and Δ¹⁴C Analysis**

All filters were sub-sampled prior to elemental and isotopic analysis. For POM悬浮 Δ¹⁴C analysis we evenly cut 1/3 of the 70mm filter for all stations except for station BB2 where 1/4 filter was used due to repeated analysis attempts. Filter subsamples were rolled and placed into pre-combusted (540°C/2h) 9mm quartz tubes with ~100mg CuO wire, evacuated to 10⁻⁷ torr on a vacuum line and sealed in 3mm Pyrex tubes for reaction. POM of sulfur in the POM sample inhibiting the graphitization condensable gas but could perhaps be due to high concentrations the sample combustion did not yield high quantities of non- further analysis. These failed attempts are difficul to explain as (McNichol and Aluwihare, 2007).

Blanks of this size are not unheard of due to the increased handling of POM samples (McNichol and Aluwihare, 2007). Since only 1/3 filter was subsampled for Δ¹⁴C analysis, an extraneous POC blank of 20.4 ± 2 μgC was assigned to all stations except for Station BB2 (1/4 filter, 15.3 μgC). This blank corresponds to approximately 10 to 16% of the total filter carbon. Blanks of this size are not unheard of due to the increased handling of POM samples (McNichol and Aluwihare, 2007). Since no nitrogen was detected on blank filters, measured POM δ¹⁵N values were not blank corrected.

**Isotopic (Δ¹⁴C and δ¹³C) Blank Correction and Error Propagation**

All POM filters contain extraneous carbon contributions associated with filter handling, sampling, and processing. To quantify a procedural blank for POM filters, we ran a blank pre-combusted 70mm QMA filter through our processing methods (including long term storage after baking). Combustion of this procedural blank yielded 61.2 ± 2 μgC. Since only 1/3 filter was subsampled for Δ¹⁴C analysis, an extraneous POC blank of 20.4 ± 2 μgC was assigned to all stations except for Station BB2 (1/4 filter, 15.3 μgC). This blank corresponds to approximately 10 to 16% of the total filter carbon. Blanks of this size are not unheard of due to the increased handling of POM samples (McNichol and Aluwihare, 2007). Since no nitrogen was detected on blank filters, measured POM δ¹⁵N values were not blank corrected.

Measured POM悬浮 Δ¹⁴C and δ¹³C values were blank corrected via isotopic mass balance (Equations 1 and 2). In all isotopic mass balances, errors were propagated following established methods (Taylor, 1997).

\[ \text{(1) } \left[ \text{POM}\text{sample} \times \Delta^{14}C_{\text{sample}} \right] + \left[ \text{POM}\text{blank} \times \Delta^{14}C_{\text{blank}} \right] \]

\[ \text{(2) } \left[ \text{POM}\text{sample} \times \delta^{13}C_{\text{sample}} \right] + \left[ \text{POM}\text{blank} \times \delta^{13}C_{\text{blank}} \right] \]

The filter procedural blank (61.2 ± 2 μgC) had a measured Δ¹⁴C value of ~801.7 ± 3.5‰. While no procedural blank was established for δ¹³C, we assumed that the only reasonable source of dead C to the filters could possibly be residual hydrocarbon
lubricant present on the Al foil during manufacturing (e.g., combusted to CO$_2$ that was subsequently absorbed by the QMA filter in its sealed Al foil envelope). Thus, we used Δ$^{14}$C and δ$^3$C blank values of −801.7 ± 3.5‰ and −28.0 ± 1.0‰, respectively in our isotopic mass balances (Cherrier et al., 2014; Walker et al., 2017). Since many of our measured POM δ$^{13}$C values were isotopically light (−25 to −29‰), this blank correction resulted in only small corrections to our measured POM δ$^{13}$C values (<0.3‰).

RESULTS

POM Concentrations, C:N$_a$ Ratios, and Fluorescence

A summary of all POM concentrations, C:N$_a$ ratios and deep chlorophyll-α maximum (DCM) fluorescence values are provided in Table 1. For simplicity, we hereafter refer to POM$_{susp}$ as ‘POM’, unless making a distinction between POM$_{sink}$ and POM$_{susp}$. We observe large ranges in POC and PON concentrations across Baffin Bay (Figures 2D, E). POC concentrations ranged from 4.1 ± 0.2 μM C L$^{-1}$ at station BB15 to 13.6 ± 0.7 μM C L$^{-1}$ at BB18, with an average value of 6.2 ± 3.0 μM C L$^{-1}$ (n=11). PON concentrations averaged 1.0 ± 0.4 μM N L$^{-1}$ (n=11) and had a smaller range – from 0.6 ± 0.1 μM N L$^{-1}$ at stations BB15, 108, 224 and 193 to 1.7 ± 0.1 μM N L$^{-1}$ at stations BB18. Excluding station BB18, which had the highest POC and PON concentrations, Eastern Baffin Bay had generally higher POC and PON values (5.6 ± 2.3 μM C L$^{-1}$ and 1.0 ± 0.3 μM N L$^{-1}$, n=5) than Western Baffin Bay (4.5 ± 0.7 μM C L$^{-1}$ and 0.7 ± 0.2 μM N L$^{-1}$, n=3), however these differences are not significant to the 95% confidence interval (2σ). Northern station (108, 323) POC concentrations (6.5 ± 0.8 μM C L$^{-1}$, n=2) were significantly higher than Western Baffin Bay.

POM C:N$_a$ ratios ranged from 7.7 to 11.2, with an average value of 9.0 ± 1.2 (n=10) (Figure 2F). We observed qualitatively higher C:N$_a$ ratios in Northern (9.5 ± 2.3, n=2) and Eastern (9.1 ± 1.1, n=5) Baffin Bay vs. Western Baffin Bay (8.5 ± 0.6, n=3). However, unlike regional POC concentrations, there was no statistically significant difference between POM C:N$_a$ when averaging Baffin Bay regions. Smith Sound (108) had the highest C:N$_a$ value (11.2). Stations with the lowest C:N$_a$ ratios (BB18, 323 and 193) had values approaching Redfield (7.7-7.8).

The DCM, as determined by a water column fluorescence maximum, was present at depths of 20-40m throughout Baffin Bay at the time of sampling. The distribution of DCM fluorescence values reveals clear differences in phytoplankton abundance across Baffin Bay. In general, Western Baffin Bay has higher fluorescence values than Eastern Baffin Bay and some elevated fluorescence values can be seen at the Northern Gateways (Figure 2C). We observe the highest fluorescence values (10-15 mg m$^{-3}$) at coastal Greenland stations adjacent to glacial fjords (Figure 2C). At sampled POM stations, fluorescence values at the DCM ranged from 0.59 mg m$^{-3}$ (193) to 11.75 mg m$^{-3}$ (BB18) with an average of 3.8 ± 3.2 mg m$^{-3}$ (n=11; Table 1). Fluorescence was high at Northern gateway stations (108, 323, 305 and 4.91 mg m$^{-3}$, respectively) and along Baffin Island at 7°N, with fluorescence decreasing into the centre of Baffin Bay from 5.64 mg m$^{-3}$ at station BB2 to 1.14 at station 224. While fluorescence had a high range in Baffin Bay, averages of our individual stations by region (East, West and Northern) did not suggest significant regional differences – at least for the POM stations we sampled.

POM$_{susp}$ δ$^{13}$C, δ$^{15}$N and Δ$^{14}$C Values

POM δ$^{13}$C and δ$^{15}$N values comprise a total range of 7.8‰ and 3.4‰, respectively (Table 1). POM δ$^{13}$C ranged from −21.6‰ at station BB18 to −29.5‰ at BB2, with an average value of −26.3 ± 2.1‰ (n=11). Negative POM δ$^{13}$C values were observed in Central-West Baffin Bay (−29.6 ± 0.8‰, n = 3). Excluding the significantly less negative POM δ$^{13}$C value from BB18, higher POM δ$^{13}$C values (−26.2 ± 0.3‰, n = 3) were present in Southeastern Baffin Bay (196, BB15, 227). POM δ$^{15}$N ranged from +3.8‰ at BB15 to +7.2‰ at 108, with an average value of...
+5.1 ± 1.1‰ (n = 10). The highest POM δ¹⁵N values were observed in the Northern gateways (108 and 323; δ¹⁵N = +6.9 ± 0.3‰, n = 2). The elevation of these Northern POM δ¹⁵N values was statistically significant (at ±2σ) from Eastern (+4.3 ± 0.5‰, n = 5) and Western Baffin Bay (+5.2 ± 0.4‰, n = 3) regions. The lowest values were observed in the Southeastern region of Baffin Bay (196, BB15, BB18, 227, δ¹⁵N = +4.1 ± 0.2‰, n = 4).

Blank-corrected POM Δ¹⁴C values span a ~119‰ range, with an average POM Δ¹⁴C value of +19.4 ± 34.6‰ (n = 10; Table 1). While 224 had the highest POM Δ¹⁴C value (+76.8 ± 15.4‰), BB2 and 204 also had very positive POM Δ¹⁴C values (+51.6 ± 18.9‰ and +54.4 ± 13.5‰, respectively). Stations 193 and 323 were the only stations with negative POM Δ¹⁴C values (~41.8 ± 9.7‰ and ~11.8 ± 9.2‰, respectively). The remaining stations (196, BB15, BB18, 227, 108; n = 5) fell in a relatively narrow Δ¹⁴C range between +2.9 ± 6.5‰ (108) and +26.1 ± 10.0‰ (196).

**DISCUSSION**

**POM Concentrations, C:Nₐ Ratios and Diagenetic State**

POC and PON concentrations were high throughout Baffin Bay (Table 1), consistent with previous studies showing high POM concentrations and rates of primary production in Baffin Bay (Lalande et al., 2009; Ardyna et al., 2011). POC and PON concentrations were not significantly correlated to SST or salinity (R² <0.0003), suggesting a biological control on the elemental composition of Baffin Bay POM. This is different from many studies showing water mass advection and upwelling as strong predictors of POM stoichiometry (e.g., Hill and Wheeler, 2002; Walker and McCarthy, 2012). Along the WGC extension, POC and PON increase from station BB15 (4.1 μM C L⁻¹; 0.6 μM N L⁻¹) to stations 227 and 204 (4.5 and 5.4 μM C L⁻¹; 0.9 and 1.1 μM N L⁻¹), respectively (Figures 2D, E). Low [POM] along the Davis Strait and Southwest Greenland shelf could be the result of nutrient limitation, as phytoplankton blooms in regions occur earlier in the year due to ice break-up (Tang et al. 2004). It is also conceivable that aged N. Atlantic waters flowing into Baffin Bay in Eastern Davis Strait are iron-limited relative to Northern Stations with high glacial influx. Increased [POC] and [PON] along the WGC extension may result from elevated micronutrient delivery from the Greenland ice sheet. For example, we observe the highest fluorescence (11.75 mg m⁻³) and POM concentrations (13.6 μM C L⁻¹, 1.7 μM N L⁻¹) at Station BB18 in the Vaigat Fjord. These high values are indicative of a local phytoplankton bloom at the time of sampling, stimulated by summer glacial discharge (Arrigo et al., 2017). Northern gateway stations (108, 323) show further increases in POC concentration (5.9-7.0 μM C L⁻¹) and fluorescence values (Figures 2C, D; Table 1).

POM concentrations decrease south of central Baffin Bay within the BIC – from BB2 (5.0 μM C L⁻¹; 1.0 μM N L⁻¹) to 224 (4.8 μM C L⁻¹; 0.6 μM N L⁻¹) and 193 (3.7 μM C L⁻¹; 0.6 μM N L⁻¹), respectively (Figure 2D). This decrease in [POM] is also reflected in decreasing DCM fluorescence values (Table 1). Whereas Stations 224 and BB2 (Western Baffin Bay) had nearly identical POM concentrations, these stations had quite different DCM fluorescence values – suggesting differences in autotrophic POM abundance at the time of sampling. Higher BB2 fluorescence values may indicate higher primary production fueled by Pacific nutrients from Lancaster Sound (Lehmann et al., 2019). Station 224 is located “downstream” in the BIC extension, possibly indicating lower POM concentrations resulting from POMdep between the BIC.

POM C:Nₐ ratios are valuable indicators of POM diagenetic state (e.g., Cowie and Hedges, 1994) and provide useful information regarding autochthonous vs. allochthonous POM contributions and POM chemical “freshness”. The stoichiometric model of Redfield describes the elemental composition of marine organic matter and can be used generally to link the production of new POM to nutrients. The ratio of carbon to nitrogen in POM produced by marine phytoplankton generally follows the Redfield ratio of 106:16:1 (C:N:P; Redfield, 1958), or ~7.7 as C:Nₐ. Deviation from standard Redfield stoichiometry can be used as an indicator of nutrient limitation, or the relative diagenetic state (i.e., chemical “freshness”) of POM. The relationship between organic matter C/N ratio and degradation state have described previously for dissolved organic matter (DOM), suspended vs. sinking POM, and marine sediments (Cowie and Hedges, 1994; Loh and Bauer, 2000; Hopkinson and Vallino, 2005; Walker and McCarthy, 2012; Walker et al., 2014; Walker et al., 2016). Here, POM with low C:Nₐ ratios (especially those approximating Redfield) represents recently produced and chemically “fresh” material. In contrast, POM with high C:Nₐ typically represents older, “degraded” POM contributions either from allochthonous sources or in situ degradation of fresh material (e.g., heterotrophic re-working of a senescent phytoplankton bloom). In this way, C:Nₐ ratios are a useful tool for evaluating the relative diagenetic state of marine POM.

In Baffin Bay, all POM C:Nₐ (7.7 to 11.2) had canonical “marine” values, equal to or higher than regular Redfield ratios (Figure 2F). The mean value of C:Nₐ in this study (9.0 ± 1.2) closely resembles POM C:Nₐ (8.9) previously reported for the Eastern Greenland shelf, in which high C:Nₐ was attributed to nitrate limitation, and the dominance of carbon-rich diatoms (Daly et al., 1999). Our POM C:Nₐ values together with observed seawater salinities, preclude significant terrestrial (C:Nₐ ~40) POM contributions. High POM C:Nₐ values (10.0-11.2) at stations 108, 204, and BB15 potentially indicate higher contributions of degraded POM. Previously work has shown POM C:Nₐ ratios in the North Water polynya (i.e., near Station 108) found C:Nₐ increases in early spring and summer with concomitant increases in irradiance and decreases in nitrate (Mei et al., 2005). Prolonged periods of high irradiance can lead to elevated POM C:Nₐ under nitrogen limitation, as phytoplankton synthesize N-poor photoprotective pigments (Levasseur and Therriault, 1987; Dubinsky and Berman-Frank, 2001). We observed Redfield POM C:Nₐ values (7.7) at three stations BB18, 323, and 193. These stations comprise a wide spatial range and are found in distinct marine ecosystems in Baffin Bay. As previously mentioned, station BB18 is in the glacial meltwater-dominated Vaigat Fjord, whereas stations 323 is in one of Baffin Bay’s Northern gateways. Surprisingly, Station
193, the southernmost extent of the BIC, had very low [POM] concentrations. Thus, while low C:N values are often associated with abundant “fresh” POM produced under nutrient-replete conditions, this is not always the case. One explanation of these data could be a non-traditional allochthonous POM$_{susp}$ source. For example, POM$_{sink}$ contributions at Station 193 could explain low C:N$_r$ and low POC concentrations. Alternatively, re-suspension and lateral advection of recently exported (“fresh”) POM from sediments could also explain this low C:N$_r$ ratio. Such re-suspended sedimentary organic carbon (SOC) contributions to POM$_{susp}$ have been observed previously in the coastal ocean (e.g., Walker et al., 2014).

**Sources of Particulate Organic Carbon and Nitrogen in Baffin Bay**

Our measured POM $\delta^{13}$C values ($-21.6\%_o$ to $-29.5\%_o$) are consistent with previous work from Baffin Bay showing the prevalence of both fast-growing plankton in glacial meltwater, in addition slow-growing phytoplankton from high latitudes with negative $\delta^{13}$C values (Goericke and Fry, 1994). Similarly, the large range in POM $\delta^{15}$N values ($-3.4\%_o$) can likely be attributed to disparate nitrate sources in Baffin Bay (Lehmann et al., 2019). For example, the advection of surface water masses (e.g., Atlantic, Arctic, Pacific/CAA) in Baffin Bay deliver allochthonous nutrients and POM$_{susp}$ to the region. While annual freshwater contributions to Baffin Bay are estimated to be 100 km$^3$ yr$^{-1}$ (Shiklomanov et al., 2021), the salinity at our stations was never below 29.6, and outside of station BB18, was always associated with the BIC (e.g., dominated by Arctic outflow water; Azetsu-Scott et al., 2012). This, combined with low POM C:N$_r$ found at all stations, precludes significant contributions of terrestrial POM affecting our $\delta^{13}$C values.

We observe several trends in POM $\delta^{13}$C and $\delta^{15}$N values in relation to surface water salinity (Figures 3A, B). Our WGC stations 196, BB15, 227, 204, and 210 have similar salinity (>32.17), $\delta^{13}$C and $\delta^{15}$N values (Figures 3A, B). WGC POM $\delta^{13}$C values are generally consistent with canonical POM $\delta^{13}$C values for high-latitude phytoplankton ($\delta^{13}$C = $-24$ to $-26\%o$; De La Vega et al., 2019). For example, excluding the most negative WGC POM $\delta^{13}$C value (204; $-27.8\%o$), the average WGC POM $\delta^{13}$C value is $-26.3 \pm 0.3\%o$ ($n = 4$). These stations similarly cluster together in $\delta^{13}$C-$\delta^{15}$N space, with an average $\delta^{15}$N$_r$ $= 4.1 \pm 0.3\%o$ ($n = 3$; Figure 3B). Thus, we conclude that for most WGC stations, POM $\delta^{13}$C and $\delta^{15}$N$_r$ values can be attributed to the prevalence of high-latitude phytoplankton utilizing the inflow of WGC and Irminger Current water as their main $\delta^{15}$NO$_3$ source (+4-6‰; Sherwood et al., 2021). Station 204 has negative POM $\delta^{13}$C ($-27.8\%o$) and positive $\delta^{13}$N$_r$ (+5.1%) values, but falls on a continuum between Atlantic WGC water to Central Baffin Bay isotopic endmembers (Figure 3B). We believe these isotopic trends between the WGC and Central Baffin Bay are due to both mixing and recycling of PON and/or NO$_3$ contributing the $\delta^{15}$N enrichment of POM.

BIC Stations (BB2, 224, and 193) have low SST (0-2°C) and salinity (S<30.54), negative POM $\delta^{13}$C ($-28.6 \pm 0.81\%o$, $n = 3$) and intermediate $\delta^{15}$N$_r$ (+5.2 ± 0.4%, $n = 3$) values (Table 1; Figures 3A, B). Negative BIC POM $\delta^{13}$C values are consistent with slow-growing, cold-water phytoplankton as a major POM source. Station BB2 has the highest $\delta^{15}$N$_r$ (+5.7%) outside of the Northern gateway stations and is influenced by the Northern BIC. Similarly, high POM $\delta^{15}$N values for Stations 224 and 193 in the BIC are likely influenced by the Pacific $\delta^{15}$NO$_3$ propagating south from Lancaster Sound. This interpretation would be consistent with recent work showing the Pacific $\delta^{15}$NO$_3$ signature is not only entrained into the BIC, but subsequently carried into the Labrador Current (Sherwood et al., 2021).

POM at the Northern gateways (323, 108) had the highest $\delta^{15}$N$_r$ values of +6.6% and +7.2% and, excluding station BB18, the highest $\delta^{13}$C values of $-25.1\%o$ and $-24.0\%o$ (Figures 3A, B). Both stations likely contain moderate contributions of sea-ice algae POM. Station 323 in Lancaster Sound is a gateway for entering Pacific water that is a precursor to the BIC ($S = 30.14$; Münchow et al., 2015). Station 323 had more positive $\delta^{13}$C ($-25.1\%o$) than other BIC stations (BB2, 224, 193; $-28.6 \pm 0.81\%o$) that can likely be attributed to seasonal variability and/or local sea-ice algae POM contributions. These results are consistent with previous Station 323 POM $\delta^{13}$C values of $-24.2\%$ reported in October 2011 that were also attributed to sea-ice algae (Roy et al., 2015). Station 108 in the Smith Sound ($S = 31.16$) comprises several water mass contributions, including the WGC, Arctic water from Nares Strait and glacial meltwater from coastal Greenland. Previous POM $\delta^{13}$C values from the North Water polynya (near Station 108) were $-22.3\%o$ and $-27.6\%o$ for samples collected in April 1998 and October 2011, respectively (Hobson et al., 2002; Roy et al., 2015). Thus, Northern Baffin Bay POM likely contains more sea-ice algae POM in spring following ice break-up, and fewer contributions of positive $\delta^{13}$C sea-ice algae in the fall ($-20$ to $-18\%o$; Hobson et al., 2002; De La Vega et al., 2019). The high POM $\delta^{15}$N$_r$ values we observe from 323 and 108 are clearly influenced by the influx of high $\delta^{15}$N Pacific nutrients (NO$_3$) entering Baffin Bay via the CAA as has been previously observed for Lancaster Sound (e.g. Lehmann et al., 2019). Together our POM $\delta^{13}$C and $\delta^{15}$N$_r$ values from station 323 and 108 suggest Pacific nutrients, a polar marine plankton and sea-ice algae as the dominant POM carbon and nitrogen sources in Northern Baffin Bay.

Station BB18 is a clear outlier in the sample set and had the highest $\delta^{13}$C value ($-21.6\%o$) and one of the lowest $\delta^{15}$N$_r$ values (+3.9%; Figures 3A, B). Station BB18 is located within the Vaigat fjord and had the lowest salinity of all coastal Greenland stations ($S = 31.40$) and highest POM concentrations. The stable isotopic signature of BB18 POM can be attributed to high phytoplankton growth in the stratified fjord waters at the time of sampling (Figure S1-4). BB18 POM $\delta^{15}$N is similar to Atlantic $\delta^{15}$NO$_3$, indicating an influx of Atlantic nitrate and high glacial meltwater delivery of iron can fuel high rates of primary production, as has been observed previously (Bhatia et al., 2013; Meire, et al., 2017).

**Disparate POM $\Delta^{14}$C Sources and Cycling Rates**

To further elucidate POM sources and cycling in Baffin Bay, here we discuss POM radiocarbon ($\Delta^{14}$C) values. Due to the short residence time of sinking and suspended POM in the water
column (days to years), POM $\Delta^{14}$C values are largely determined by carbon sources as opposed to ages via radioactive decay. Possible POM $\Delta^{14}$C sources in Baffin Bay are: i) modern surface and pre-aged, upwelled DIC used in primary production, ii) modern or pre-aged allochthonous POM contributions advected from other regions, iii) modern or “bomb” terrestrial POM, iv) pre-aged glacial meltwater, v) re-mobilization of ancient permafrost and vi) pre-aged re-
suspended SOC. Marine POM with Δ14C values similar to that of surface DIC Δ14C indicates a prevalence of in situ primary production as a major POM source (e.g., POM with a higher proportion of phytoplankton-derived, autochthonous POM) and POM Δ14C values that fall outside the range of DIC Δ14C could indicate allochthonous POM contributions with pre-aged (negative Δ14C) or “bomb” (positive Δ14C) signatures.

The ~119‰ range in POM Δ14C values we observe throughout Baffin Bay is both striking and somewhat unexpected given the overall “freshness” of POM samples (i.e., generally low C:N ratios, high POM concentrations) and their stable isotopic composition largely indicating planktonic carbon and local nutrient sources (Figures 2, 3). This range in surface POM Δ14C values is also especially high for a single oceanographic region. For example, the range in POM Δ14C values we observe exceeds the range previously reported from an intense California upwelling system (~101‰; Walker et al., 2014). Whereas most POM Δ14C samples fall within the range of measured surface DIC Δ14C values, four of our POM Δ14C values fall outside this range – indicating allochthonous POM contributions (Figure 3C).

Three stations (BB2, 224, 204) had higher Δ14C values (> ±2σ) than surface DIC Δ14C (Figure 3C). Stations BB2 and 224 are in the central gyre, with Δ13C of +51.6±18.9‰ and +76.8±15.4‰, respectively. Station 204, near coastal Greenland, had Δ13C of +54.5±13.5‰. Measured surface DIC Δ14C values for BB2, 224, and 204, are +5.6‰, +14.1‰, and +14.2‰, respectively (errors ±1.5‰; Zeidan et al., 2022). This large disparity between DIC Δ14C and POC Δ14C indicates the clear presence of allochthonous POM with an atmospheric “bomb” Δ14C signature within central Baffin Bay. These positive POM Δ14C values likely arise from POM contributions that were synthesized during periods of high atmospheric Δ14C. This would require POM in central Baffin Bay to be decades old. Atmospheric Δ13C CO2 was last at +80‰ approximately 16 years before our sampling (e.g., between 2001-2003; Levin et al., 2010) and marine DIC reached this value in the 1970’s (Druffel, 1996). Thus, our results suggest that a portion of the POMsamp pool may be retained in the central gyre of Baffin Bay and possibly recycled in the surface for several decades. Additional sources of bomb Δ14C could be advected POM from the North Atlantic (+100 to +140‰ in 1992; Druffel et al., 1992), or via the CAA (Beaufort Sea DIC Δ14C = +82‰ in 2012; Druffel et al., 2017). However, neither our Northern nor Southern gateway stations (323, 108, 193, 196) contained highly positive POM or DIC Δ14C values. In addition, POM δ15N values from these three stations (~28.5 ± 0.9‰) are consistent with slow-growing, cold-water phytoplankton from higher latitudes (Holding et al., 2017). Thus, it is more likely that these cold-water phytoplankton, along with some pre-existing bomb Δ14C persisting in the central gyre, are responsible for our observed POM Δ14C and δ15N values in central Baffin Bay. Lastly, station 204 on the north-central Greenland shelf, more closely resembles BIC stations isotopically (Δ13C, Δ14C, δ15N), suggesting a similar POM source to central Baffin Bay at the time of sampling. Surface admixture of WGC waters with surface water from the gyre as evidenced from its lower salinity value (32.17) relative to other WGC stations (>32.9) is a distinct probability.

We observe a highly negative POM Δ14C value at station 193 (~41.8±9.7‰). This POM Δ14C value is significantly different from surface in situ DIC Δ14C (+15.6‰; Zeidan et al., 2022). As mentioned above, this sample had the low POM concentrations and C:N. We believe contributions of resuspended SOC to Station 193 POM the be the most reasonable explanation of these data. SOC contributions to POM are now widely recognized as a common pathway through which 14C-depleted carbon can be transported laterally from the coastal ocean and incorporated into the POM pool (Rau et al., 1986; Druffel et al., 1992; Druffel et al., 1996; Druffel et al., 1998; Hwang et al., 2005; Hwang et al., 2010; Walker et al., 2014). SOC δ13C values for the Arctic average ~22‰ to ~26‰, with end-member values being ~27 to ~28‰ (Drenzek et al., 2007; Magen et al., 2010; Roy et al., 2015). Thus, the Station 193 δ13C value of ~28.0‰ is plausible. Additionally, C:N (wt/wt) ratios of sediments from the Bering and south Chukchi seas showed open shelf sediments generally had C:N less than 7 (Naïdu, et al., 1993). The C:N ratio for station 193 when calculated by weight is 6.7. From these multiple lines of evidence, we hypothesize POM at station 193 contains resuspended SOC contributions, albeit perhaps recently exported, “fresh” SOC with a low C:N. Future work on the shelf/slope of Davis Strait could target re-suspended sediment POM contributions through the use of %AI or sedimentary biomarker measurements.

While the deviation of POM Δ14C from in situ DIC Δ14C values reveal an interesting diversity of Baffin Bay POM sources and cycling, most of our POM Δ14C fall within the range of measured surface DIC Δ14C (Figure 3C). All these samples are from WGC (196, BB15, 227, BB18), or the Northern gateway (108, 323) stations. Here, POM Δ14C values are statistically indistinguishable from in situ DIC Δ14C (+ ±2σ). The similarity of POM and DIC Δ14C values at these locations has important implications for carbon cycling within Baffin Bay. For example, these data suggest that most of the de novo POM synthesis in Baffin Bay occurs along coastal Greenland fueled by Atlantic macronutrients (nitrate) and glacial micronutrients (iron). This primary production largely governs export production within Baffin Bay. With future climate change scenarios indicating warming of Baffin Bay and enhanced Greenland ice sheet melting, favoring large centric diatoms, and extended ice-free conditions (Krawczyk et al., 2021), it stands to reason that these regions of Baffin Bay will continue to support most POM export and burial in Baffin Bay.

**SUMMARY AND IMPLICATIONS**

As a detrital organic matter reservoir, POMsamp represents a complex geochemical mixture of non-living materials. The chemical composition of POM does not always match that of resident plankton communities and can be strongly influenced by pre-aged, allochthonous POM contributions. The bulk elemental and isotopic composition of POM presented in this
study provides us with a new understanding of the sources, diageneric state, and the geochemical impact of POM in Baffin Bay. These first POM $\Delta^{14}$C data, together with $\delta^{13}$C and $\delta^{15}$N suggest a diversity of POM carbon and nitrogen sources in Baffin Bay. Overall, POM isotopic $\delta^{13}$C, $\delta^{15}$N, and $\Delta^{14}$C signatures are controlled by surface water mass circulation, local algal communities and nutrient sources, and to a lesser extent, contributions from allochthous POM sources. Primary production fueled by Atlantic nitrate is a major source of new POM in Eastern Baffin Bay. In particular, the coastal fjords along Greenland are unique, high-productivity environments decoupled from the broader surface circulation-driven POM trends. The Northern gateways, through which Arctic and Pacific waters flow into Baffin Bay, also show considerable POM contributions from in situ production from both high latitude phytoplankton and sea-ice algae utilizing Pacific nitrate. Stations in central Baffin Bay are strongly influenced by the cold and fresh BIC, with POM contributions mainly from slow-growing cold water phytoplankton again fueled by Pacific nitrate entering Baffin Bay via the CAA.

Measured POM $\Delta^{14}$C values add to this emerging picture of POM cycling in several ways. First, POM $\Delta^{14}$C within the WGC and Northern gateways matches that of in situ DIC $\Delta^{14}$C, suggesting that primary production results in $^{14}$C-modern POM in these regions. In this way, these regions serve as the primary drivers POM export and carbon cycling in Baffin Bay. Second, POM with highly positive $\Delta^{14}$C values is found in the central gyre – indicating the presence of bomb $^{14}$C. POM synthesized in the western Canadian Arctic (i.e., Beaufort Sea) and advected through the CAA represents a possible source of positive POM $\Delta^{14}$C to Baffin Bay. Other possibilities could include recycling of bomb $^{14}$C within the central Baffin Bay POM$_{\text{susp}}$ reservoir or influx of terrestrial POM. However, stable isotopic ($\delta^{13}$C, $\delta^{15}$N) signatures and C:N$_{\text{a}}$ ratios do not support the latter. The former scenario would necessitate the decadal persistence of a recalcitrant POM$_{\text{susp}}$ fraction in the gyre. None of these scenarios have simple explanations and further work is required to confirm the persistence of bomb $^{14}$C in central Baffin Bay. Finally, POM exiting Baffin Bay via the western Davis Strait has highly negative $\Delta^{14}$C values. Together with [POC], [PON] and C:N$_{\text{a}}$ data, we believe resuspended sediments were a major contributor to this POM sample. Such contributions are supported by previous geochemical and global $^{14}$C studies of the POM pool. The export of POM with negative $\Delta^{14}$C values has important implications for the geochemical impact of the BIC on the Labrador Sea. If entrained in North Atlantic Deep Water during its formation, this could represent a previously unrecognized source of $^{14}$C-depleted POM to the deep ocean.

POM isotopic ($\Delta^{14}$C, $\delta^{13}$C, $\delta^{15}$N) data remain sparse for this region, yet provide invaluable baseline data for evaluating carbon and nitrogen cycling in a rapidly changing Arctic region. Future work focused on increasing the spatial resolution of POM $\Delta^{14}$C observations, together with compound-class or compound specific isotopic analysis, would improve our understanding of the cycling of fresh vs. recalcitrant POM components in Baffin Bay. These measurements have proven useful in parsing out individual allochthonous POM components, such as contributions from resuspended sediment (e.g., Roland et al., 2008).

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

BW conceived the hypothesis and the objectives of this investigation. BW collected the POM samples at sea. AF processed the samples in the lab for isotopic analysis with BW. AF wrote the manuscript with input from BW. All authors contributed to the article and approved the submitted version.

FUNDING

Funding for this project was provided by the Natural Sciences and Engineering Research Council (NSERC) of Canada through a Discovery Grant, Accelerator and Launch Supplements (RGPIN-2020-06501, RGPAS-2020-00071, DGECR-2020-00256; to BW). A portion of this work was supported through the Canada Research Chairs program (to BW).

ACKNOWLEDGMENTS

We would like to thank Chief Scientist Alexandre Forest, Anissa Merzouk and the staff of Amundsen Science and the crew of the CCGS Amundsen for the opportunity to participate in the 2019 research cruise and for providing CTD data. We thank Drs. Cara Manning and Brent Else for their help in coordinating the sampling and logistics of the Biogeochemistry groups aboard the CCGS Amundsen. We thank Drs. Xiaomei Xu and John Southon of the UC Irvine Keck Carbon Cycle AMS lab for their expertise and help with $^{14}$C analysis of our graphite targets and GB-IRMS $\delta^{13}$C measurements. We thank Colin Carney at UC Santa Cruz for additional POM stable isotope ($\delta^{13}$C, $\delta^{15}$N) measurements.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmars.2022.846025/full#supplementary-material
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