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Sources and sink of black carbon in Arctic Ocean sediments

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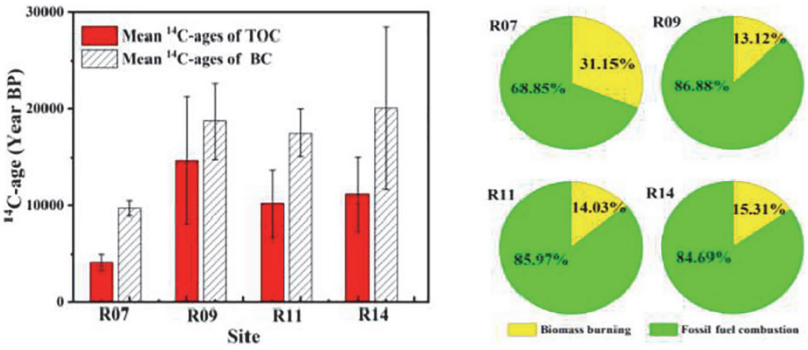
HIGHLIGHTS

- Black carbon (BC) accounted for 3.5% to 15.2% of the TOC preserved in the Arctic Ocean sediments.
- The ^{14}C ages of BC are 4093–7723 years older than the age of TOC.
- Fossil fuel combustion and biomass burning contributed 62–96% and 4–38% of the BC in the Arctic Ocean sediments.
- BC represents a significant sink of atmospheric CO_2 and global carbon cycle in the Arctic Ocean.

GRAPHICAL ABSTRACT



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ABSTRACT

The concentrations and carbon isotopic (^{13}C, ^{14}C) compositions of total organic carbon (TOC) and black carbon (BC) were measured for four sediment cores collected from the shelf to slope in the Arctic Ocean. Contents of TOC and BC ranged from 0.46% to 1.94% and 0.04% to 0.13% by dry weight, and BC accounted for 3.5% to 15.2% of the TOC preserved in the shelf and slope sediments. Sediment of the Chukchi shelf contained relatively high BC contents compared with the sediments of the Arctic slope, suggesting strong influence from the river and terrestrial inputs to the shelf region. Radiocarbon measurements revealed that the ages of BC are in the range of 7330 to 29,700 years (before present) and they are 4093 to 7723 years older than the ^{14}C ages of TOC preserved in the same sediment depths. Based on an isotopic mass balance model, we calculated that fossil fuel combustion contributed 62–96%, and biomass burning contributed 4–38% of the BC pool in the sediments of the study area. This “slow-cycling” old BC is an important fraction of the inert organic carbon pool preserved in the sediments, and represents a significant sink of atmospheric CO_2 and global carbon cycle. With the thawing permafrost caused by continuous global warming, the size of this BC pool mobilized and exported by rivers to the Arctic Ocean could increase in the future.

1. Introduction

Black carbon (BC) is a highly refractory residue from incomplete combustion of fossil fuels and biomass (Goldberg, 1985; Masiello, 2004). Due to its very stable aromatic chemical structure, BC has an

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extremely long environmental lifetime and is dispersed ubiquitously in the natural environment, especially in soils and marine sediments (Laflamme and Hites, 1978; Gustafsson and Gschwend, 1998; Masiello and Druffel, 1998; Glaser and Amelung, 2003; Smith et al., 2010). Once preserved in sediments, BC is resistant to microbial degradation and thus can serve as a useful marker for past environmental changes (Verardo and Ruddiman, 1996; Marlon et al., 2008; Sun et al., 2008). The residence time of BC in oceanic and terrestrial settings could be as long as several million years, which has a large impact on both regional and global climate through their effect on Earth's radiative balance (Verardo and Ruddiman, 1996; Schmidt et al., 2001; Druffel, 2004; Elmquist et al., 2008; Shrestha et al., 2010).

Previous studies have shown that global emissions produce about 12–24 Tg ($1\ \text{Tg} = 1 \times 10^{12}$ g) BC from fossil fuel combustion (Penner et al., 1993), and 50–270 Tg BC from biomass burning annually (Kuhlbusch and Crutzen, 1995; Kuhlbusch, 1998), which could account for a significant proportion of the "missing carbon" in the global C budget (Druffel, 2004). It has been estimated that about $9.64\ \text{Tg}\cdot\text{y}^{-1}$ and $0.63\ \text{Tg}\cdot\text{y}^{-1}$ BC were buried in continental shelf and open ocean sediments, and BC buried in continental shelf sediments accounted for 90% of the total amount of BC buried in marine sediments (Suman et al., 1997). Compared with the major global carbon reservoirs, BC preserved in marine sediments is a small fraction of the total, but studies have showed that this small "slow-cycling" BC pool could be an important sink in the global biogeochemical cycle of carbon (Masiello and Druffel, 1998; Verardo and Ruddiman, 1996; Wang et al., 2005; Marlon et al., 2008). Studies have shown that BC often represents a significant fraction of the organic carbon preserved in the sediments, largely depending on the environmental setting (Schmidt et al., 2001; Bianchi et al., 2002; Druffel, 2004; Wang and Li, 2007; Shrestha et al., 2010). For example, Masiello and Druffel (1998) reported that BC accounted for 15% and 21% of TOC preserved in the deep sediments of the Northeast Pacific Ocean and the South Atlantic Ocean, respectively. Middelburg et al. (1999) also reported 15–30% of the TOC in the sediments of the North Atlantic was BC. A study by Verardo and Ruddiman (1996) once reported a surprisingly high BC content that accounted for 50% of the sedimentary TOC in the Eastern equatorial Atlantic. In large river-influenced marginal seas, the preservation of BC in sediments usually accounts for a significant fraction of sedimentary TOC, reflecting the export of terrestrial BC by rivers. Kang et al. (2009) reported that the BC content accounted for 27–41% of the sedimentary TOC in the highly contaminated Bohai Bay, and 6–14% of TOC in sediments of the less contaminated Yellow Sea and East China Sea, respectively. Combustion of fossil fuel, especially coal, contributed the most BC (60–80%) to the sediments of China's river-influenced marginal seas (Wang and Li, 2007).

Few studies have investigated the preservation of BC in sediment of the Arctic Ocean. Studies by Guo et al. (2004) and Elmquist et al. (2008) have found that the distribution of BC in the sediments of the Arctic Ocean also varied greatly, with higher values (17%) in the coastal areas influenced by rivers and much lower values (<1%) in central Arctic areas unaffected by rivers. In a recent study, Yang and Guo (2018) reported that the soot-BC contents averaging 1.6 ± 0.3, 0.46 ± 0.04 and 0.56 ± 0.10 mgC/g, accounted for 16.6%, 10.2% and 10.4% of the TOC preserved in the surface sediments on the Mackenzie, Chukchi and Bering Shelves in the Arctic. The Arctic Ocean has a large continental shelf region with the greatest input of freshwater than any other ocean, thus making the Arctic the most sensitive region to global climate change and ecosystem changes caused by global warming (Cuffey et al., 1995; Manabe and Stouffer, 2000; Marris et al., 2015). Studies have shown that rivers are the major sources of BC to the ocean (Dittmar et al., 2012; Jaffé et al., 2013; Wagner et al., 2015; Wang et al., 2016; Coppola et al., 2018). Considering the wide and frequent vegetation fires in the circum-Arctic region (Kozlov et al., 2008; Boike et al., 2016) and large drainage basins of the Arctic rivers, a large amount of BC could be transported by rivers into the Arctic Ocean (Guo et al., 2004; Elmquist et al., 2008). Salvadó et al. (2017) recently estimated that the total burial flux of soot BC in the East Siberian Arctic Shelf sediments could reach ~4000 Gg yr^{-1}, thus representing an important sequestration of BC in the ocean.

Radiocarbon measurements of BC hold promise for identifying the sources and fate of BC in the environment (Druffel, 2004). BC produced from biomass burning has a $\Delta^{14}C \geq 0‰$ with modern ages, whereas BC produced from fossil fuel combustion has a $\Delta^{14}C = -1000‰$ as dead carbon (Stuiver and Polach, 1977; Masiello and Druffel, 1998). Studies have shown that BC preserved in marine sediments has a wide range of radiocarbon ages, therefore representing different sources and time scales of cycling. Masiello and Druffel (1998) reported that BC preserved in the sediments of the North Pacific and Atlantic oceans had ^{14}C ages ranging from 2400 to 13,900 years, much older than the non-BC sedimentary TOC deposited concurrently. In the Arctic region, Elmquist et al. (2008) and Guo et al. (2004) found increasing ^{14}C ages of sedimentary TOC from the west (Ob River) to the east (Kolyma River) and calculated that the contribution from modern biomass burning to BC ranged from low in the Yukon (8%) and Lena (5%) rivers to high in the Yenisei river (88%). In their recent study, Salvadó et al. (2017) reported more depleted and uniform ^{14}C signatures (average $-774 \pm 62‰$) of soot BC than of non-BC sedimentary TOC in the East Siberian Arctic Shelf. The very old BC (5900 ± 300 yrs) deposited in the sediments was mainly derived from the remobilization of thawing permafrost carbon, rather than atmospheric input (Guo et al., 2007; Feng et al., 2015; Salvadó et al., 2017). However, the sources and preservation of BC in Arctic shelf and slope sediments, especially with depth, have not been well investigated. In this study, we applied carbon isotopic (^{13}C, ^{14}C) measurements to constrain and reveal the preservation and sources of BC in the sediments of the Arctic Ocean and quantitatively determined the contribution of fossil fuel combustion and biomass burning to the BC pool preserved in the sediments of the Arctic Ocean.

2. Materials and methods

2.1. Sample collection

Four sediment cores were collected from the Arctic Ocean (Fig. 1), using a box core sampler on board the *R/V* Xuelong during the cruise of the sixth Chinese National Arctic Research Expedition in summer (July–August) of 2014. One core (R07) was collected on the Chukchi shelf and three cores (R09, R11 and R14) were collected on the slope of the Arctic Ocean (Fig. 1), with water depths varying from 73 m to 742 m. All sediments were dominated by silt/clay, with variable sedimentation rates (Table 1). After collection, the sediment cores were capped, kept frozen, and transported back to the laboratory. The cores were sectioned at 1 cm intervals in the laboratory and kept frozen until further processing.

2.2. Measurement of grain size, total organic carbon (TOC) and total nitrogen (TN)

Grain size of the sediments was measured according to Fang et al. (2015). Briefly, freeze-dried unground sediment was reacted with 0.25 M HCl and 30% H_2O_2 overnight to remove carbonate and organic matter, and then rinsed 3 times with Milli-Q water to remove the extra HCl and H_2O_2. The sediment was then fully dispersed by ultrasonic oscillation and grain size was measured using a Mastersizer 2000 Laser (Malvern Panalytical). The mean grain size is presented as Φ ($\Phi = -\log_2 D$, D is the grain size diameter in mm) (Fang et al., 2015; Cai et al., 2017).

For TOC measurement, freeze-dried sediments were first acidified with 2 M HCl at room temperature for 24 h to remove inorganic carbon. Then they were rinsed to neutral pH with Milli-Q water, dried (55 °C) and ground to powder. The carbonate-free sediment samples were measured for TOC and TN in duplicates using an Elemental Analyzer

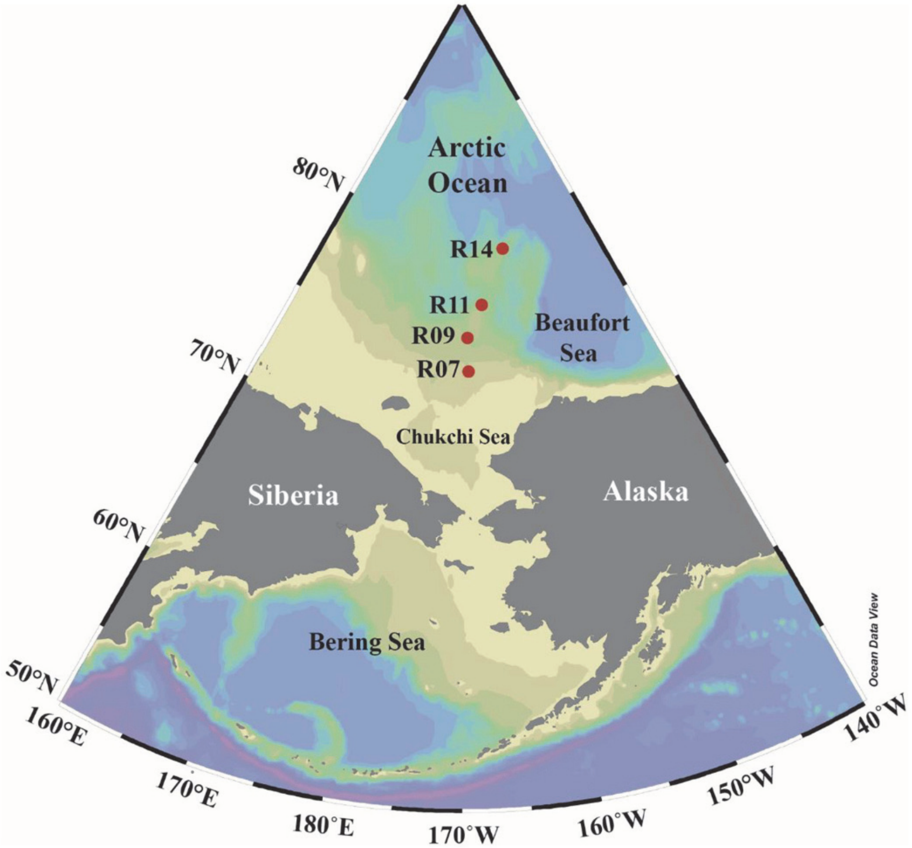

Fig. 1. Map showing the sampling sites of the four sediment cores collected in the Arctic Ocean. The general information about the sampling sites is summarized in Table 1.

(Thermo Fisher Flash 2000), with a standard deviation of ±0.02% for TOC and ± 0.04% for TN(n = 6).

2.3. BC separation

The separation of BC from complex natural samples is still a challenge (Hammes et al., 2007). There is no single fixed method used in previous studies. For separation of BC in soil and marine sediments, chemothermal oxidation (CTO) and chemical oxidation (CO) techniques have been the two most commonly used methods (Gustafsson et al., 1997; Masiello and Druffel, 1998; Reddy et al., 2002; Guo et al., 2004; Hammes et al., 2007; Wang and Li, 2007; Salvadó et al., 2017). Previous studies have shown that both methods are reproducible and precise. The CTO method mainly measures the soot-BC and graphitic-BC fractions (Cachier et al., 1989; Gustafsson et al., 1997; Gélinas et al., 2001) and the CO method measures the charcoal-BC and soot-BC fractions (Wolbach and Anders, 1989; Gillespie, 1990; Verardo, 1997). In our study, we applied the CTO method (Gustafsson et al., 2001) to separate BC from sediments because this requires no chemicals added to the samples during treatment, so possible contamination for carbon isotope (^{13}C, ^{14}C) measurements was minimal. Also, our results can be compared with the recent BC studies conducted for Arctic sediments using the same CTO method (Salvadó et al., 2017; Yang and Guo, 2018). We also compared the CTO method and CO method as modified by Masiello et al. (2002) for BC separation and isotope measurements.

For the CTO method, about 200 mg carbonate-free finely ground sediment was placed in thin even layer (1–2 mm) in a petri dish, and heated at 375 °C for 24 h in an oven with a continuous air supply. This method operationally defines the organic carbon that remained after this oxidation step as BC (Gustafsson et al., 1997; Elmquist et al., 2004). After the CTO separation step, sediment was placed in 9 mm OD quartz tubes (pre-combusted at 850 °C for 2 h) with CuO and Ag wire added and combusted at 850 °C for 2 h. The resultant CO_2 from BC oxidation was collected cryogenically and quantified manometrically on a vacuum line. The purified CO_2 was flame sealed in a 6 mm OD glass tube for further isotopic analysis. The blanks associated with this method were very small (<2 μg C, n = 6). For the CO method, according to the TOC content, a certain amount of carbonate-free sediment (~3 g) was placed into a 50 ml Teflon centrifuge tube. Sediment was treated with 10 M HF/1 M HCl mixed solution at 60 °C for 24 h to

Table 1
General information of the sampling sites of the four sediment cores in the Arctic Ocean.

Sediment core	Sampling location	Sampling date	Water depth/m	Core depth/cm	Sedimentation rate/mm·a^{-1}	Sediment type
R07	168.97°W;73.00°N	July–August, 2014	73	30	0.84[a]	Silt/clay
R09	169.03°W;74.61°N		184	36	0.44[a]	Silt/clay
R11	166.20°W;76.15°N		343	46	0.6[b]	Silt/clay
R14	160.43°W;78.63°N		742	26	0.012[c]	Silt/clay

[a] Data from Astakhov et al. (2019).
[b] Data from Yu et al. (2012).
[c] Data from Mei et al. (2012).

remove silicate. Then, 10 M HCL was added to the Teflon centrifuge tube and reacted at 60 °C for 24 h. After the reactions, sediment samples were washed with Milli-Q water several times to remove calcium and fluoride ions, and then dried at 60 °C. About 100–300 mg dried sediment was weighed into each Teflon tube (50 ml) and then oxidized using a 0.1 M $K_2Cr_2O_7$/2 M H_2SO_4 mixed solution at 55 °C for 60 h to oxidize organic matter. After the oxidation, sediments were washed with Milli-Q water three times and dried again at 60 °C. Organic carbon left after the oxidation step was defined as BC (Verardo, 1997; Masiello et al., 2002) and the content was measured by quartz tube combustion and quantified on the vacuum line as described above.

2.4. Measurement of $\delta^{13}C$ and $\Delta^{14}C$

Carbon isotope compositions (^{13}C and ^{14}C) were measured for both sediment TOC and BC. Sample $\delta^{13}C$ was measured using a Thermo 253 Plus Isotope Ratio Mass Spectrometer (IRMS) coupled with an Elemental Analyzer in the Center for Isotope Geochemistry and Geochronology (CIGG) at Qingdao National Laboratory for Marine Science and Technology (QNLM) in Qingdao, China. Values of $\delta^{13}C$ are reported in ‰ relative to the IAEA ^{13}C standards, and the analytic precision was <0.2‰ ($n = 10$). Sample $\Delta^{14}C$ was measured by accelerator mass spectrometry (AMS) after graphitization of sample CO_2 in the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility at Woods Hole Oceanographic Institution (WHOI) and the AMS facility of CIGG at QNLM. All $\Delta^{14}C$ measurements were reported as fraction modern (FM) and the conventional radiocarbon ages (year before present) were calculated using the Libby half-life as ascribed by Stuiver and Polach (1977).

3. Results

The results of all measurements are summarized in Table S1 in the Supplementary Information of this paper. The results indicate that the two methods used for BC separation, CTO and CO, are comparable. For the 8 samples we tested, the BC concentrations are 0.060 ± 0.02% and 0.054 ± 0.02%, and the $\Delta^{14}C$ values are −851 ± 70‰ and −881 ± 73‰ as determined by the CTO and CO methods respectively. The concentration of BC and its $\Delta^{14}C$ values determined by the CTO method were slightly higher than those determined by the CO method, consistent with the results of Masiello and Druffel (1998). This could suggest that some of the refractory non-BC organic matter was not fully removed at 375 °C by the CTO method, thus resulting in slightly higher BC and $\Delta^{14}C$ values.

3.1. Sediment characteristics

The grain sizes of the sediment cores R07, R09, R11 and R14 ranged from 4.4 to 4.8 Φ, 4.6–5.8 Φ, 4.8–5.7 Φ, and 5.4–6.7 Φ with an average of 4.6 ± 0.1 Φ, 5.5 ± 0.4 Φ, 5.2 ± 0.3 Φ and 6.3 ± 0.4 Φ, respectively (Table S1). In general, the grain sizes increased slightly with depth in the cores and core R14 had relatively larger grain sizes than the other three cores. The contents of TOC and TN ranged from 0.46 to 1.94% and 0.08–0.18% by dry weight for the four sediment cores (Table S1), and core R07 collected in the Chukchi Sea shelf region had the highest TOC values (1.11–1.94%). TOC contents in the other three cores were all <1.0%. As plotted in Fig. 2, the TOC profiles in cores R07, R09 and R11, in general, all decreased with depth, but decreased in the surface and then increased with depth down to 25 cm in core R14 (Fig. 2d). In comparison, the TN contents were much lower (<0.3%) and exhibited constant profiles

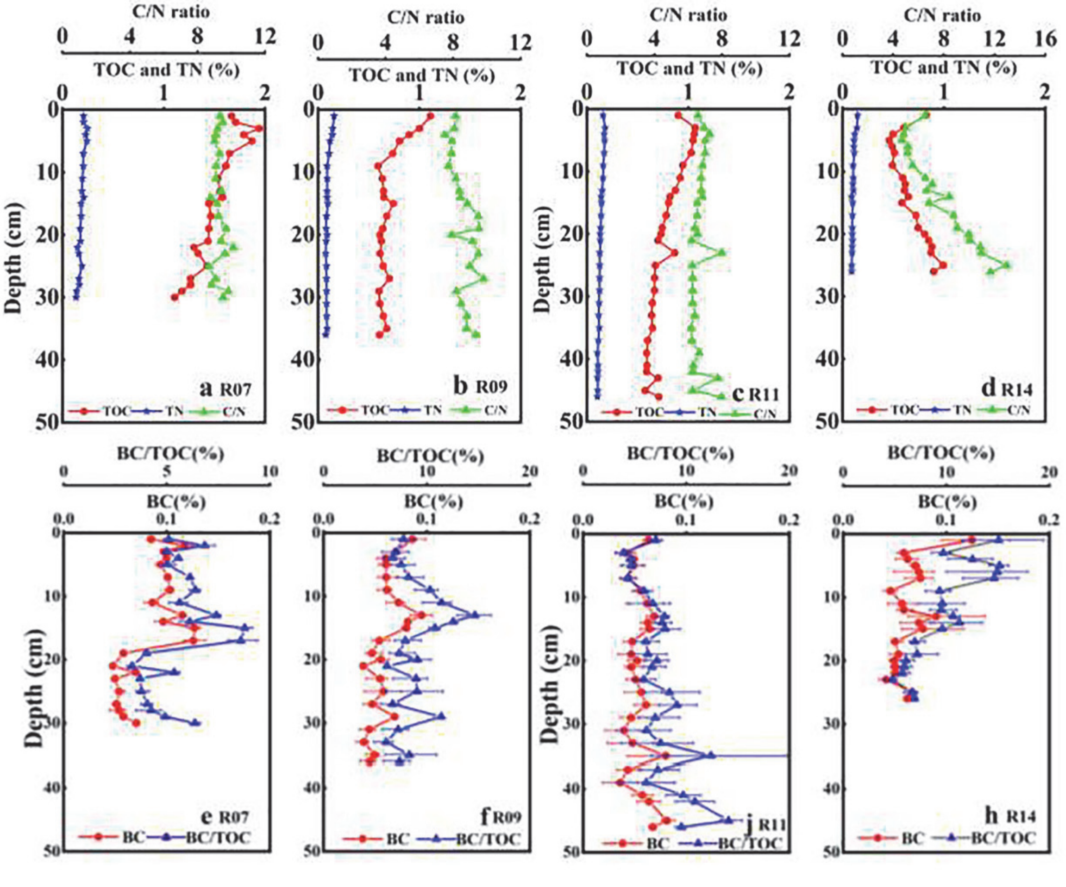

Fig. 2. Plots of (a–d) the depth distributions of TOC (%), TN (%), and C/N ratios; (e–h) BC (%) and BC/TOC (%) ratios in the four sediment cores collected from the Arctic Ocean.

in the four sediment cores (Fig. 2). The calculated C/N molar ratios ranged from 6.1 to 12.8 for the four cores with average values of 9.3, 8.5, 6.7 and 7.9 for cores R07, R09, R11 and R14, respectively (Table S1). The C/N profiles in the sediments were relatively constant for cores R07, R09 and R11, and increased with depth in core R14 (Fig. 2).

3.2. Contents of black carbon

The contents of BC measured ranged from 0.05 to 0.13%, 0.04–0.09%, 0.04–0.08% and 0.04–0.12% (by dry weight) for cores R07, R09, R11 and R14, respectively (Table S1). As plotted in Fig. 2e–h, the distribution of BC in the cores showed some variations with depth. The average BC content was slightly higher (0.08%) in core R07 than the other three cores. The calculated BC/TOC ratios indicate that BC accounted for 3.5–9.0%, 6.2–13.9%, 3.7–13.9% and 4.6–15.2% of the TOC in cores R07, R09, R11 and R14, respectively, with average values of 5.6%, 8.6%, 7.5% and 10.0%. Core R14 had relatively higher BC/TOC ratios and core R07 had the lowest BC/TOC ratios among the cores. In general, the profiles of BC and the ratio of BC/TOC showed parallel distributions with depth in the sediment cores (Fig. 2e–h).

3.3. Carbon isotopic signatures of TOC and BC

The results of carbon isotopic values (δ^{13}C and Δ^{14}C) measured for TOC and BC in the four sediment cores are summarized in Table S1. Values of δ^{13}C-TOC ranged from −22.7‰ to −23.8‰ for R07, −22.2‰ to −25.0‰ for R09, −21.7‰ to −25.2‰ for R11 and −22.5‰ to −26.5‰ for R14, with average values of −23.2‰, −24.1‰, −22.7‰ and −25.1‰ for each core respectively. In comparison, values of δ^{13}C-BC measured in the same cores ranged from −20.9‰ to −23.0‰, −21.3‰ to −23.4‰, −20.8‰ to −24.0‰ and −20.9‰ to −24.6‰, with average values of −21.8‰, −22.2‰, −21.8‰ and −23.2‰ for each core. As shown in Fig. 3, the depth distributions of δ^{13}C-BC values in the four sediment cores are all higher than the δ^{13}C-TOC values. Except for core R07, the δ^{13}C-TOC values decreased with depth and δ^{13}C-BC values showed some variations, decreased with depth in cores R11 and R14, and increased slightly in core R07 (Fig. 3a–d).

Values of Δ^{14}C-TOC measured in the four sediment cores ranged from −337‰ to −529‰ in R07, −428‰ to −936‰ in R09, −493‰ to −869‰ in R11 and −455‰ to −868‰ in R14, with average values of −405‰, −782‰, −699‰ and −719‰ for each core (Table S1). In comparison, values of Δ^{14}C-BC measured in the same cores ranged from −653‰ to −742‰, −794‰ to −957‰, −835‰ to −928‰ and −602‰ to −976‰, with average values of −702‰, −893‰, −883‰ and −863‰ for cores R07, R09, R11 and R14, respectively. As plotted in Fig. 3e–h, Δ^{14}C-TOC values all decreased with depth and their ^{14}C ages increased with depth from the surface. The Δ^{14}C-BC values were all lower than the Δ^{14}C-TOC in the four sediment cores, and they also decreased with depth especially in core R14 (Fig. 3h). The ages of BC were much older than the ages of TOC in the sediments, especially in the surface layers (0–1 cm) in cores R07, R09 and R11 (Fig. 3). The ages of BC were 9450, 12,600, 14,400, and 7330 years (BP) compared with the ages of TOC of 3240, 4430, 5850 and 4800 years (BP) in the surface sediment of cores R07, R09, R11 and R14. The ages of BC were 2530–8550 years older than the ages of TOC.

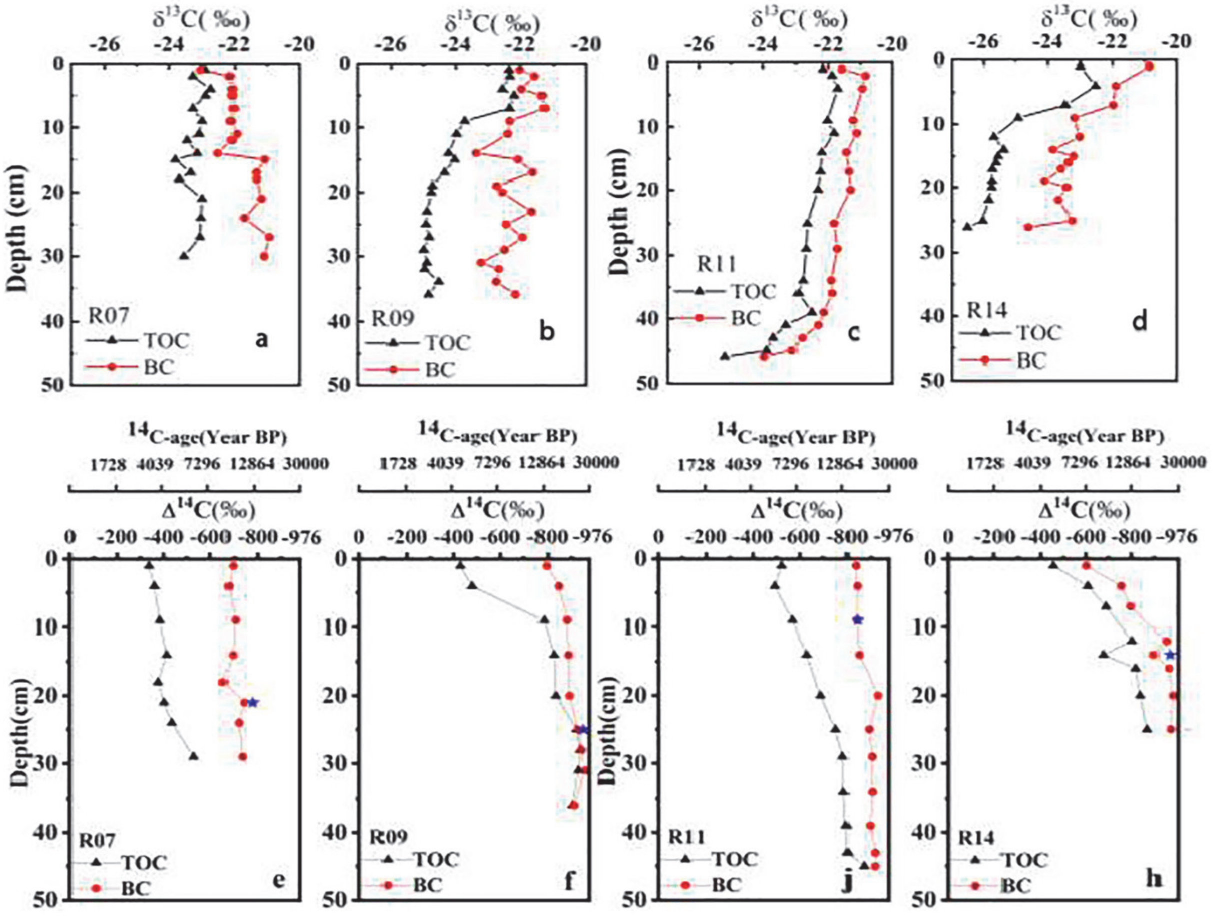

Fig. 3. Plots of (a–d) depth distributions of δ^{13}C, and (e–h) Δ^{14}C and ^{14}C ages (year before present) measured for TOC and BC in the four sediment cores collected from the Arctic Ocean.

4. Discussion

4.1. Preservation of OC in the Arctic Ocean sediments

The concentrations of OC preserved in the four sediment cores showed a general decrease from the Chukchi Sea shelf (R07, 1.51%) to the Arctic slope (R14, 0.69%), consistent with the results of some recent studies conducted in the same Arctic region (Marris et al., 2015; Feng et al., 2015; Salvadó et al., 2017). For the four cores we studied, we see a decrease of TOC% with increasing grain sizes in the sediments as plotted in Fig. 4a ($R^2 = 0.80$). Core R07 with small grain sizes had higher TOC% (1.51%) than core R14 (0.69%). This pattern indicates that the fine sediment particles of R07 such as clay minerals have high specific surface areas and adsorption capacity for OC, as demonstrated in many other marine sediments (Hedges, 1978; Wang and Lee, 1993; Keil et al., 1994; Mayer, 1994; Curry et al., 2007; Keil and Mayer, 2014). The strong adsorption of OC onto fine mineral surfaces could also protect OC from microbiological degradation, thus preserving OC in the sediments (Keil et al., 1994; Keil and Mayer, 2014).

Studies have shown that the Chukchi Sea and the Beaufort Sea of the western Arctic Ocean are sensitive areas undergoing significant climate change in recent decades, influenced greatly by increasing river discharge and thawing permafrost associated with coastal erosion, and increased productivity of the water column due to decreased sea ice coverage (Guo et al., 2007; Fichot et al., 2013; Feng et al., 2015; Marris et al., 2015). In their recent study of stable carbon and nitrogen isotopes of sedimentary OM, Marris et al. (2015) estimated that 50–70% of the OC buried in the surface shelf sediments of the western Arctic Ocean was from water column productivity, 25–35% was from sea ice algal production, and 15% was from rivers. The ^{13}C values we measured for sedimentary TOC in the four cores showed a mixture of both marine-derived and terrestrial OC sources. The higher TOC% and relatively constant $\delta^{13}C$-TOC (~−23.2‰) depth distributions in core R07 (Fig. 3a) could suggest rapid deposition of OM in the sediments and good preservation by the fine clay minerals in the shelf of the Chukchi Sea. The sedimentation rates measured by Astakhov et al. (2019) for core R07 (0.84 $mm \cdot y^{-1}$) was significantly higher than cores R09 (0.44 $mm \cdot y^{-1}$), R11 (0.60 $mm \cdot y^{-1}$) and R14 (0.012 $mm \cdot y^{-1}$) (Mei et al., 2012; Yu et al., 2012). From the shelf to slope, $\delta^{13}C$-TOC values are clearly enriched in the surface sediments compared with the deep layers for the other three cores, especially for cores R09 and R14 (Fig. 3b, d). The $\delta^{13}C$-TOC values that are enriched in the surface and decreasing with depth could suggest deposition of a large fraction of marine-derived OM in the inner shelf and slope region of the Arctic Ocean in recent decades (Gradinger, 2009; Marris et al., 2015) and rapid degradation of this newly deposited fresh OM in the sediment surface, resulting in the accumulation of more refractory terrestrial OC being preserved with depth in the sediments. In their earlier studies, Guo et al. (2007) and Gaye et al. (2007) reported that the $\delta^{13}C$ values of particulate organic carbon (POC) transported by the three Alaskan rivers (Mackenzie, Sagavanirktok and Yukon) ranged from −28.9‰ to −26.3‰ and the $\delta^{13}C$ values of TOC in the surface sediments along the Siberian Arctic coastline, including the Ob, Yenisei, Khatanga, Lena and Indigirka estuaries ranged from −27.6‰ to −23.8‰ (Guo et al., 2004), comparable with the values we measured for TOC in the sediment cores below the surface layer (Fig. 3a–d).

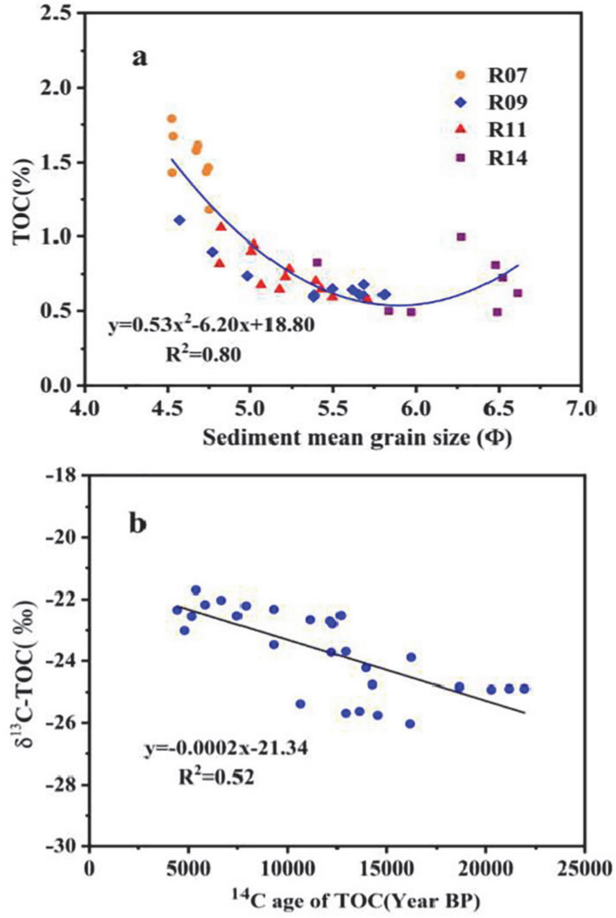

Fig. 4. Plot of (a) TOC% vs. sediment mean grain size (Φ), and (b) $\delta^{13}C$-TOC (‰) vs. ^{14}C ages of TOC for the four cores collected in the Arctic Ocean. The line is a (a) polynomial fit and (b) linear regression fit to the data.

The rapid degradation of marine-derived OC in the surface sediments in the Arctic Ocean is strongly supported by the $\Delta^{14}C$-TOC signatures in the sediment cores (Fig. 3e–h). In the very surface (0–1 cm), the TOC ages reached 3240, 4430, 5850 and 4800 years for R07, R09, R11 and R14, respectively. These very old TOC ages suggest that the marine-derived recently-fixed OM deposited on the surface sediment was respired and the majority of TOC was likely from pre-aged refractory permafrost OC mobilized and transported by the Arctic rivers to the ocean (Guo et al., 2004; Goni et al., 2005; Guo et al., 2007; Fichot et al., 2013; Feng et al., 2015). In their recent study, Salvadó et al. (2017) also reported broad-ranging, old ^{14}C ages of TOC (2680–10,800 years) in the surface sediments of the East Siberian Arctic shelf. They concluded that the old TOC was mainly from thawing permafrost and exported from the rivers. As plotted in Fig. 4b, a general correlation ($R^2 = 0.52$) between $\delta^{13}C$-TOC and TOC ages in the three cores (R09, R11 and R14) exists, showing that values of $\delta^{13}C$-TOC decreased with the increase of TOC ages in the slope sediments, indicating the nature of the terrestrial-origin permafrost OC that was more resistant to microbiological degradation and preserved in the sediment with depth. Another possibility is that the very old TOC preserved in the cores R09, R11 and R14 could be influence by hydrocarbon (HC) seeps in these sediments. In our continued study, we measured ^{13}C and ^{14}C for HC extracted from these cores and found very depleted $\delta^{13}C$ values (−28.0‰ to −29.9‰) and old ^{14}C ages (8860–25,920 years) for HC (unpublished data), suggesting the possible existence of hydrocarbon seeps in these sediments similar as reported in other marine sediments (Wang et al., 2001; Valentine et al., 2005).

4.2. Distribution and sources of BC in the sediment

The BC content in the four sediment cores is in good agreement with the results reported by other studies for the Arctic Ocean. In their recent study using the same CTO method, Salvadó et al. (2017) reported soot-BC concentrations ranging from 0.1 to 2.1 $mg \cdot g^{-1}$, accounting for 2–12% of the TOC preserved in the surface sediments of the East Siberian Arctic shelf. More recently using the same CTO method, Yang and Guo (2018) measured BC concentrations averaging 1.6 ± 0.3, 0.46 ± 0.04, and 0.56

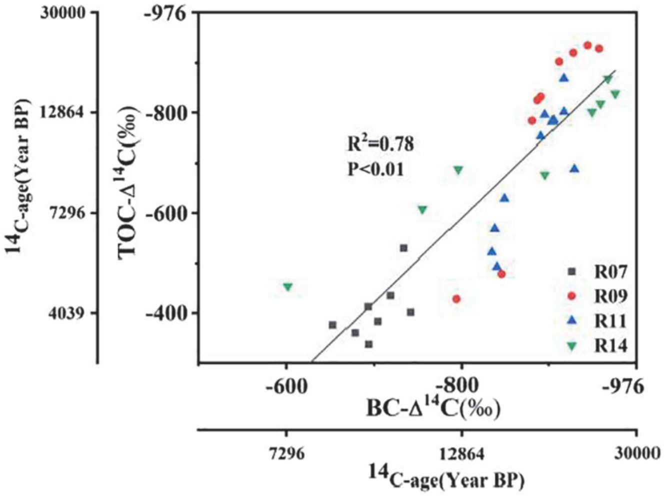

Fig. 5. Plot of the calculated ^{14}C ages of BC vs. ^{14}C ages of TOC in the four sediment cores collected in the Arctic Ocean. The line is a linear regression fit to the data.

± 0.10 mg·g^{-1}, accounting for 16.6%, 10.2% and 10.4% of the TOC preserved in the surface sediments in the shelves of Mackenzie, Chukchi and Bering seas, respectively. The average BC contents we measured are constant within a relatively small range of 0.6–0.8 mg·g^{-1} and accounted for 5.6–10.2% of the TOC buried in the four sediment cores. These similar results suggest that the CTO method is reliable and reproducible for BC separation in sediments, as suggested previously (Gustafsson et al., 2001; Reddy et al., 2002; Hammes et al., 2007).

The carbon isotope signatures of BC showed an interesting comparison with TOC in the sediment cores. The values of δ^{13}C-BC are all more enriched than δ^{13}C-TOC (Fig. 3). The reason for enrichment of δ^{13}C in BC is not clear but could suggest the same source of BC. In their study, Yang and Guo (2018) also measured very consistent δ^{13}C values for soot BC in each Arctic sediment core they studied. The calculated ^{14}C ages of BC (average: 9708, 18,705, 17,543 and 20,056) are all much older than the ages of TOC (average: 4128, 14,686, 10,235 and 11,990) in the four cores, especially in core R07 (Fig. 3e–h), consistent with the results of Salvadó et al. (2017), indicating that the BC preserved in the Arctic Ocean sediments was from very old refractory sources. As plotted in Fig. 5, a good linear correlation ($R^2 = 0.78$, $p < 0.01$) exists between the ages of TOC and BC in the sediments indicating that BC was deposited proportionally with TOC in the sediments and both decays away in parallel with time at depth.

Sources of BC in modern sediments include fossil fuel combustion, biomass burning and rock weathering (Druffel, 2004; Masiello et al., 2002) and these different sources of BC can be identified with their ^{14}C signatures. In their study, Elmquist et al. (2008) reported a wide range of Δ^{14}C-BC values, from +51‰ to −905‰ in pan-Arctic sediments. The contribution of pre-aged carbon to surface sediments has been observed in the Mackenzie River and Yukon River. In contrast, river drainage regions with frequent large forest fires such as the Yenisey River had relatively modern ^{14}C age OM (Guo et al., 2004; Elmquist et al., 2008). Using an isotopic mass balance model, we calculated the contributions of both fossil fuel combustion and biomass burning to the BC pool preserved in the four sediment cores in the Arctic. The model is based on the following equations (Masiello and Druffel, 1998):

$$\Delta^{14}C_{sample} = f_B\,\Delta^{14}C_B + f_F\,\Delta^{14}C_F \quad (1)$$

$$f_B + f_F = 1 \quad (2)$$

where $\Delta^{14}C_{sample}$ is the measured ^{14}C value of BC at each depth, and $\Delta^{14}C_B$ and $\Delta^{14}C_F$ represent the ^{14}C values of BC from fossil fuel combustion and biomass burning. And f_B and f_F represent the fraction of BC generated from fossil fuel combustion and biomass burning, respectively. BC from fossil fuel combustion contains no radiocarbon and thus has a Δ^{14}C value of −1000‰, and BC from biomass burning should have a modern Δ^{14}C value, and here we assign it to be +50‰ (Masiello and Druffel, 1998; Wang and Li, 2007). However, once BC was buried in the sediment, its ^{14}C will decay with time so it is necessary to correct for the decay time with the sedimentation rate below the surface. So, we corrected the values of $\Delta^{14}C_{sample}$ based on the formula:

$$\Delta^{14}C_{sample} = \left[FM \times e^{\lambda\,(1950-T)} - 1\right] \times 1000 \quad (3)$$

$$T = Tc - \text{deposition depth/sedimentation rate} \quad (4)$$

where FM is the measured ^{14}C fraction modern, T is the year of deposition, Tc is the year of sample collection, $\lambda = 1/8267$.

The calculated results are plotted in Fig. 6. Clearly, fossil fuel combustion (which includes weathered rock recalcitrant OC) was the major source, contributing 62% to 96% of BC preserved in the sediments. Modern biomass burning contributed less, at 3.6% to 38% of the sedimentary BC pool, to the four sediment cores. The content of BC from biomass burning generally decreased with depth in cores R09, R11 and R14. These results are in good agreement with the data reported in previous studies (Guo et al., 2004; Elmquist et al., 2008; Salvadó et al., 2017), suggesting that fossil fuel-origin BC was mainly exported by rivers from

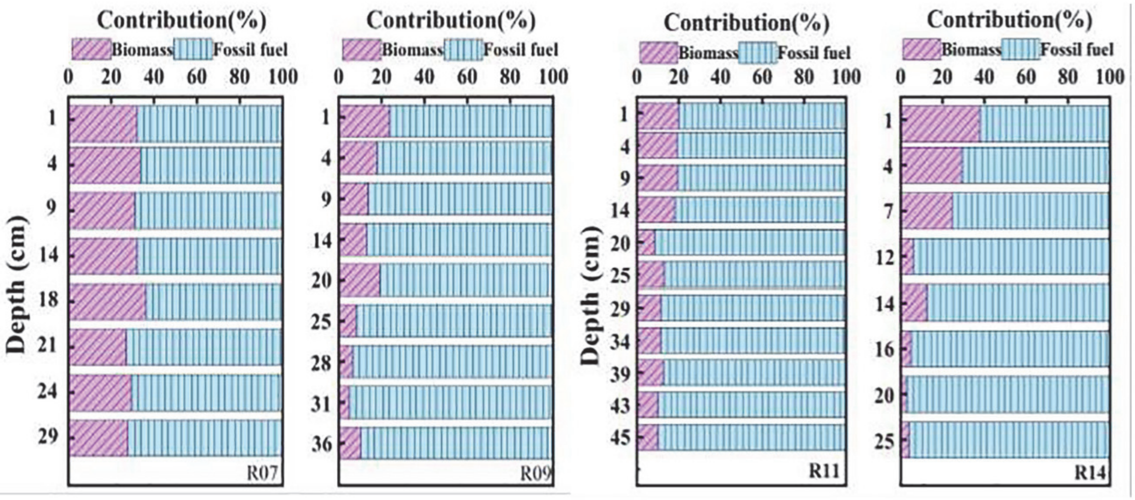

Fig. 6. Calculated contributions of fossil fuel combustion and biomass burning to the BC pool with depth in the four sediment cores collected from the Arctic Ocean.

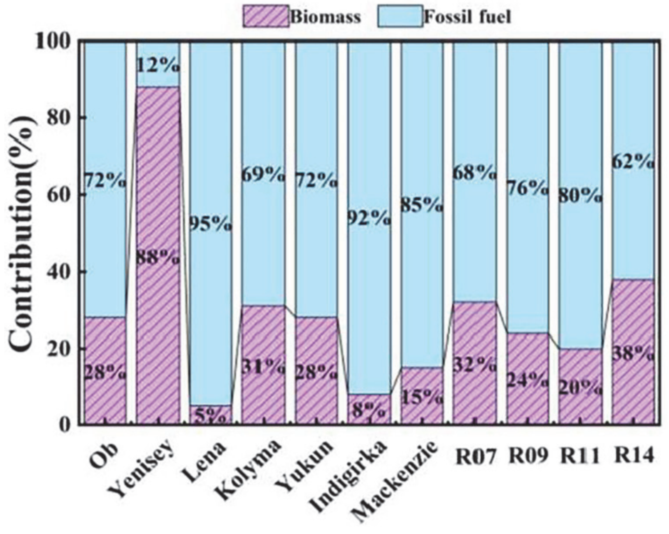

Fig. 7. The contribution of fossil fuel combustion and biomass burning to the BC in the surface sediments of the seven largest Artic river estuaries in the pan-Arctic continental shelf. River data are from Elmquist et al. (2008).

thawing permafrost. The BC contribution from aerosol deposition was very small in the Arctic region (Marris et al., 2015; Salvadó et al., 2017). Of course, BC produced from biomass burning and preserved in the permafrost could also be aged with time, but not likely changing the value back by several thousand years as seen here. However, some recent studies have addressed the importance of BC emissions in Russia in recent years. Evans et al. (2017) estimated that total BC emissions from Russia was 688 Gg in 2014. This large BC emission could increase the aerosol deposition of BC to the Arctic Ocean (Kholod and Evans, 2016; Evans et al., 2017). More studies on the influence of aerosol deposition of BC in the Arctic region are certainly needed.

Arctic rivers play an important role in mobilization and export of BC from land to the coastal regions. The contribution from fossil fuel combustion and modern biomass burning to the BC pool in the four sediment cores we studied are comparable to the values determined by Elmquist et al. (2008) for the seven Arctic rivers. As compared in Fig. 7, all rivers except for the Yenisey export higher BC content (72–95%) from fossil fuel combustion than from biomass burning (5–32%), consistent with the values we calculated for the BC pool in the sediments. It is estimated that the three Arctic shelves could bury >3000 Gg of soot-BC each year (Yang and Guo, 2018); therefore, the Arctic Ocean plays an important role as a sink of atmospheric CO_2 in the global carbon cycle.

5. Summary

Four sediment cores collected from the shelf to slope in the Arctic Ocean showed differences in contents of TOC and BC. Higher TOC was associated with small grain sizes in the Chukchi Sea sediments and decreased offshore in the slope sediments of the Arctic Ocean. BC was distributed in all sediments and accounted for 3.5% to 15.2% of the TOC preserved in the sediments with slightly higher values in the shelf than in the slope sediments. The $\delta^{13}C$ and $\Delta^{14}C$ values indicate that the majority of TOC preserved in the sediments was old and likely from pre-aged refractory permafrost OC mobilized and transported by Arctic rivers to the ocean. The ages of BC were much older than those of the TOC. A calculation based on an isotope mass balance model indicates that fossil fuel combustion contributed the majority (62–96%) of BC and modern biomass burning contributed 3.6–38% of the BC preserved in Arctic sediments. With global warming continuing to cause permafrost thawing in the Arctic, the sink of river-exported permafrost TOC and BC in Arctic sediments could increase, and the significance of refractory BC in the global carbon cycle needs to be further studied.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.06.437.

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