

## Advances in Chinese and international biogeochemistry research in the western Arctic Ocean: a review

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**Abstract** Over the past decades, the Arctic Ocean has experienced rapid warming under climate change, which has dramatically altered its physical and biogeochemical properties. Reduction in the sea-ice cover is one of the most important driving forces of biogeochemical changes in the Arctic Ocean. Between 1999 and 2016, seven Chinese National Arctic Research Expeditions have taken place in the Bering and Chukchi seas, allowing assessment of the biogeochemical response of the western Arctic Ocean to global warming. Herein, we summarize advances in Chinese and international marine biogeochemistry research in the western Arctic Ocean, reviewing results from the Chinese expeditions and highlighting future trends of biogeochemistry in the Pacific Arctic region. The findings reported in this paper contribute towards a better understanding of water masses, greenhouse gases, nutrients, ocean acidification, and organic carbon export and burial processes in this region.

**Keywords** Arctic Ocean, biogeochemistry, fresh water input, nutrients, phytoplankton, organic carbon, greenhouse gases, ocean acidification

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### 1 Introduction

The Arctic Ocean is the smallest of the world's five major oceans: it is approximately 4000 km long and 2400 km wide. It lies entirely within the Arctic Circle, contains deep basins (with an average depth of 4500 m), and about 15% of the world's shelf seas (Menard and Smith, 1966). Over the past decades, global warming and climate change have dramatically altered the Arctic Ocean's physical and biogeochemical properties in ways previously unseen.

These changes have occurred in a relatively short period of time, and include: rapid sea-ice retreat (Perovich and Richter-Menge, 2009; Johannessen et al., 1999); increase in sea surface temperature (Steele et al., 2008), freshwater storage (Giles et al., 2012; Morison et al., 2012), primary production (Arrigo and van Dijken, 2011), and Pacific water inflow (Zhuang et al., 2016; Woodgate et al., 2012); changes in sea-air carbon dioxide (CO<sub>2</sub>) fluxes (Evans et al., 2015; Gao et al., 2012; Cai et al., 2010; Mucci et al., 2010; Semiletov et al., 2007; Bates, 2006; Bates et al., 2006; Murata and Takizawa, 2003), nutrient dynamics (Li et al., 2015; Zhang et al., 2015; Bates et al., 2014; Zhuang et al., 2011), the biological pump (Coupel et al., 2012; Jiao et al.,

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2010), terrigenous carbon input (Wang et al., 2017; Xu et al., 2017), and carbon burial (Yu et al., 2012).

Because the Arctic Ocean plays an important role in the global carbon cycle and budget, it is essential to understand the consequences of the changes taking place here. The Arctic Ocean carbon budget was dominated by the transport of inorganic carbon in 1998, when Anderson et al. (1998) found a slightly larger oceanic transport coming into the Arctic Ocean, compared to the one going out. The budget calculation and comparison between years is important to understand the effects of a climatic perturbation on the physical, biological, and microbial carbon pumps, as well as on the carbon sink and source in the Arctic Ocean.

Since 1999, seven Chinese National Arctic Research Expeditions (CHINAREs-Arctic) have been carried out onboard the Icebreaker R/V *Xuelong* during the summers of 1999, 2003, 2008, 2010, 2012, 2014, and 2016. The expeditions took place in the Bering Sea, the Chukchi Sea, and the Canada Basin, where upper ocean nutrients are abundant compared with the European sector of the Arctic Ocean. Seawater, particulate matter, and sediments, were sampled and analyzed for nutrients, dissolved oxygen, pH, partial pressure of CO<sub>2</sub> (*p*CO<sub>2</sub>), phytoplankton, particulate organic carbon, dissolved inorganic carbon (DIC), total alkalinity (TA), stable isotopes of carbon, nitrogen and oxygen (<sup>13</sup>C, <sup>15</sup>N, <sup>18</sup>O), greenhouse gases (CO<sub>2</sub>, methane—CH<sub>4</sub>, and nitrous oxide—N<sub>2</sub>O), and biogeochemical parameters such as opal and biomarkers.

In recent years, Chinese biogeochemistry research groups have provided new data on the western Arctic Ocean, which had been poorly investigated until now. These new data have improved our understanding of water-mass mixing, oceanic uptake of anthropogenic CO<sub>2</sub>, ocean acidification, nutrient dynamics, phytoplankton response, and distribution of greenhouse gases in the water column, organic carbon fluxes, and carbon burial in sediments. The aim of this paper is to review the work of the Chinese and the international community investigating the Arctic, highlighting the progress that has been made in the field of Arctic biogeochemistry research.

## 2 Water masses and fresh water input indicated by chemical tracers

The principal waters entering the Arctic Ocean are from the North Atlantic (via Fram Strait and Barents Sea) and the North Pacific (via Bering Strait) (McLaughlin et al., 1996). There are two varieties of relatively warm summer halocline water in the vicinity of the Chukchi Sea: the fairly fresh Alaskan Coastal Water (ACW), and the saltier summer Bering Sea Water (sBSW), which, as its name implies, is heated and freshened in the Chukchi Sea during summer. There is also one type of winter Pacific halocline water: the

winter Bering Sea Water (Steele et al., 2004). The ACW is comparatively warmer, strongly influenced by river runoff (especially from the Yukon River), and has relatively low salinity (between 31 and 32). The sBSW is cooler, unaffected by runoff, and has a higher salinity (between 32 and 33) (Steele et al., 2004). The circulation of Pacific halocline waters seems to be strongly influenced by the surface stress forcing associated with changes in atmospheric climate modes (Steele et al., 2004). During strongly positive phases of the Arctic Oscillation (i.e., between the late 1980s and early 1990s), the ACW flows through the western Canadian Arctic Archipelago, and the sBSW flows through the Nares and Fram straits (Steele et al., 2004). When the Arctic Oscillation is weak, both types of water are incorporated into an expanded Beaufort Gyre (Steele et al., 2004).

Freshwater plays a dynamic role in the global climate by affecting the heat exchange between air, ice, and ocean (Carmack, 2000). It may also significantly affect the circulation in the Arctic Ocean, as well as convective processes in the North Atlantic (Proshutinsky et al., 2002; Aagaard and Carmack, 1989), because fluctuations in freshwater export influence the depth and volume of deep water formation in the North Atlantic and ultimately the strength of the global thermohaline circulation (Proshutinsky et al., 2002). The largest amount of freshwater, which includes sea-ice melt water, river water, and low-salinity Pacific water that flows through the Bering Strait (Steele et al., 2004), is stored in the Beaufort Gyre in the Canada Basin. The southern Canada Basin receives enhanced river runoff from the Mackenzie River, whereas the central Canada Basin receives runoff from the Yukon River via the Alaska Coastal Current, or from the Kolyma River in Russia via the East Siberian Coastal Current (Pan et al., 2014).

The Arctic Ocean receives more water in precipitation and runoff than that it loses in evaporation (Carmack, 2000). The main source of freshwater for the Canada Basin is the Pacific inflow through the Bering Strait (Tong et al., 2017), although melting of sea ice also freshens the Arctic Ocean (Johannessen et al., 1999). The addition or removal of freshwater to or from this ocean has a major effect on ocean dynamics: its upper layers are salt- rather than temperature-stratified, which provides it with the vertical stability required to allow the formation of a sea-ice cover (Carmack, 2000), as heat transfer is inhibited from the deep ocean to the surface (Shimada et al., 2006). To understand the fate of pollutants, nutrients, and marine processes in the Arctic Ocean, it is crucial to understand the sources, distributions, and pathways of the freshwater components (Cai et al., 2010; Yamamoto-Kawai et al., 2008).

The isotopic composition of river water is highly depleted in <sup>18</sup>O relative to marine waters and sea ice (Pan et al., 2014), which is why fractions of freshwater components (river runoff, RW; and sea-ice melt water, SIM) in seawater can be deduced from associating salinity with the oxygen

isotope ratio  $\delta^{18}\text{O}$  (a conservative tracer) (Tong et al., 2017, 2014; Pan et al., 2015, 2014; Macdonald et al., 2002; Bauch et al., 1995). Sea-ice formation and melting have little effect on  $\delta^{18}\text{O}$  in seawater, but considerably alter salinity (Pan et al., 2014). The significant difference between river runoff and sea-ice melt water in  $\delta^{18}\text{O}$  allows the two types of freshwater to be identified individually (Pan et al., 2014). Using  $\delta^{18}\text{O}$  to study the freshwater component fractions in this area, it has been estimated that over 3200 km<sup>3</sup> of freshwater comes from Pacific water (1700 km<sup>3</sup>) and meteoric water (more than 1500 km<sup>3</sup>) every year, while less than 900 km<sup>3</sup> of freshwater is removed by sea-ice formation (Yamamoto-Kawai et al., 2008). Pacific water is the saline end-member for waters with salinity less than or equal to 33, while a mixture of Pacific and Atlantic waters is the end-member for waters with salinity greater than 33 (Yamamoto-Kawai et al., 2008). It is estimated that total river water in the Canada Basin was higher than in other Arctic seas during the summers of 2003 and 2008, pointing to the importance of the Canada Basin as a main storage region for river water in the Arctic Ocean (Tong et al., 2017, 2014). During the same period, RW and SIM were more abundant in the permanent sea-ice zone than in the region where sea ice had just melted. The fractions of total, Atlantic, and Pacific RWs increased northwards to the north of 82°N, indicating the probable existence of an additional source of river water in the permanent sea-ice zone of the northern Canada Basin (Tong et al., 2017). This extra river water could possibly be accounted for by the lateral advection of shelf waters by the Transpolar Drift (Tong et al., 2017). These data suggest that sea-ice melt water also accumulates in the permanent sea-ice zone, as melt water from previous seasons is transported by the Beaufort Gyre and becomes trapped in the permanent sea-ice zone (Tong et al., 2017, 2014). Changes in the Arctic Oscillation index have been related to temporal variations in river runoff, suggesting that freshwater reserved in the Canada Basin is affected by surface sea-ice drift and water-mass movement driven by atmospheric circulation (Pan et al., 2014). Between 1967 and 2010, the Canada Basin showed a gradual decrease in river runoff from the south to the north (Pan et al., 2014), with river runoff maximum fractions every 5 to 16 years (Pan et al., 2014).

Between 2003 and 2012, eastern regions of the Bering Strait under the influence of the ACW showed depleted levels of  $\delta^{18}\text{O}$ , low salinity, warmer temperatures, and higher RW fractions. Western regions under the influence of Anadyr Water (AW) showed high  $\delta^{18}\text{O}$ , high salinity, and lower SIM fractions (Pan et al., 2015). In regions under the influence of the ACW, the effect of ACW on RW fractions was twice as great as that of the Bering Sea Water (BSW) and AW; RW fractions were regulated by interannual variations of the Yukon River discharge. In regions affected by the BSW and ACW, SIM fractions were similar; they were controlled by the interannual variation of sea-ice cover in the Bering Sea (Pan et al., 2015), and were approximately 45%

higher than SIM fractions in the regions affected by AW. On average, the freshwater passing through the Bering Strait was composed of 46% RW and 54% SIM. Over the study period, fraction ratios of RW to SIM have increased in the regions affected by the ACW, the BSW, and the AW, indicating that freshwater components in the Pacific inflow also play a role in the melting of sea ice in the Arctic Ocean (Pan et al., 2015).

Recent years of oceanographic research in the Arctic have contributed to a better understanding of the physical and chemical characteristics of water masses flowing into the Arctic Ocean via Fram and Bering Straits. However, further studies are still needed to help us better understand the consequences of global warming on the melting of summer sea ice and freshwater input into the Arctic Ocean.

### 3 Greenhouse gases sources and sinks

Greenhouse gases absorb and re-emit infrared radiation, continuously warming the Earth's surface and atmosphere. They include CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub>, and other gases. Emission of large quantities of CO<sub>2</sub> from anthropogenic activities that have taken place since the industrial revolution have greatly increased the concentrations of greenhouse gases in the atmosphere (Ciais et al., 2013).

The warming of the Earth's ocean and atmosphere has decreased the sea-ice cover in the Arctic, opening up a larger surface for gas exchange to occur between the sea and the air. In the Arctic Ocean, shelf-surface/mixed-layer seawater  $p\text{CO}_2$  is generally low (from less than 10.1325 to 30.3975 Pa) relative to atmospheric  $p\text{CO}_2$  (from approximately 39.7194 to 40.3274 Pa) (Evans et al., 2015; Bates et al., 2014). Remnant winter water on the shelf and deep waters of the Canada Basin have higher and much larger ranges of seawater  $p\text{CO}_2$  (from approximately 30.3975 Pa to greater than 60.7950 Pa) (Bates et al., 2014), while deeper waters (particularly halocline waters of the Canada Basin) have the highest  $p\text{CO}_2$  values (up to 131.7225 Pa) (Bates et al., 2014). However, there appears to be a spatial seasonality in CO<sub>2</sub> fugacity dominated by differences between the three main water masses in the Barents Sea (Atlantic Water, Arctic Water, and Coastal Water) (Lauvset et al., 2013).

Winter/early-spring water and deep Canada Basin water on the Chukchi Shelf exhibit narrow ranges of DIC and TA values; they range from approximately 2200 to 2300  $\mu\text{mol}\cdot\text{kg}^{-1}$  for DIC, and from approximately 2250 to 2350  $\mu\text{mol}\cdot\text{kg}^{-1}$  for TA (Bates et al., 2014). In summer, shelf waters exhibit wider ranges of DIC and TA values, ranging from 1850 to 2300  $\mu\text{mol}\cdot\text{kg}^{-1}$  for DIC, and from 1850 to 2350  $\mu\text{mol}\cdot\text{kg}^{-1}$  for TA (Bates et al., 2014). In the surface/mixed-layer, DIC and TA exhibit smaller ranges, from approximately 1800 to 2000  $\mu\text{mol}\cdot\text{kg}^{-1}$  for DIC, and from 1850 to 2250  $\mu\text{mol}\cdot\text{kg}^{-1}$  for TA, over a salinity range of 6. These shelf waters have high levels of dissolved oxygen (from ~350 to over 450  $\mu\text{mol}\cdot\text{kg}^{-1}$ ) and low levels

of nitrate (less than  $3 \mu\text{mol}\cdot\text{kg}^{-1}$ ), reflecting the uptake of nitrate in support of primary and new production, which, in turn, generates oxygen (Arrigo et al., 2012; Bates et al., 2006; Hill and Cota, 2005).

Shelf-surface/mixed-layer seawater on the Chukchi Shelf has a relatively high pH (from  $\sim 8.2$  to  $8.5$ ), while deeper waters have lower pH ( $< 7.8$ ) (Bates et al., 2014). As pH in the open ocean is typically around  $8.1$  to  $8.2$ , the relatively high pH of surface water on the Chukchi Shelf reflects the impact of high rates of primary production on  $\text{CO}_2$ -carbonate chemistry (Bates et al., 2014). It has been shown for the Chukchi Sea (Bates and Mathis, 2009) and other marine environments that photosynthetic uptake of  $\text{CO}_2$  leads to increases in pH, owing to adjustments of the  $\text{CO}_2$  equilibrium in seawater (Dickson et al., 2007; Zeebe and Wolf-Gladrow, 2001).

Areas of the western Arctic coastal ocean are considered as some of the strongest coastal ocean sink regions for atmospheric  $\text{CO}_2$  (Laruelle et al., 2014; Bates, 2006). A number of strong driving forces act in combination to allow absorption of  $\text{CO}_2$  from the atmosphere: undersaturation of  $\text{CO}_2$  relative to the atmosphere in summer, increased  $\text{CO}_2$  solubility in cold waters, retreat of sea-ice cover, moderate to strong winds, and high rates of primary production (Evans et al., 2015; Bates and Mathis, 2009; Bates, 2006; Bates et al., 2006; Murata and Takizawa, 2003; Pipko et al., 2002). In the western Arctic coastal ocean, maximal uptakes take place from August to October ( $-70$  to  $-10.9 \text{ Tg C}\cdot\text{a}^{-1}$ ) (Evans et al., 2015; Laruelle et al., 2014), with each of the marginal seas exhibiting different absorption rates. The Chukchi Sea absorbs large amounts of atmospheric  $\text{CO}_2$  ( $-47.6$  to  $-186.3 \text{ Tg C}\cdot\text{a}^{-1}$ , assuming an area of  $2.9 \times 10^{11} \text{ m}^2$  for the Chukchi Sea) (Evans et al., 2015; Gao et al., 2012; Semiletov et al., 2007; Bates, 2006), while the Beaufort Sea absorbs a more moderate amount of atmospheric  $\text{CO}_2$  ( $-4.4$  to  $-46.6 \text{ Tg C}\cdot\text{a}^{-1}$ , assuming an area of  $9.2 \times 10^{11} \text{ m}^2$  for the Beaufort Sea) (Evans et al., 2015; Else et al., 2013; Mucci et al., 2010). The Barents Sea is one of the strongest  $\text{CO}_2$  sinks in the Arctic region (Bates and Mathis, 2009) ( $-9.2$  to  $-67.2 \text{ Tg C}\cdot\text{a}^{-1}$  (Fransson et al., 2001)): it is undersaturated in  $\text{CO}_2$  year-round because of strong biological activity, heat loss (Omar et al., 2007), and wind speed (Lauvset et al., 2013). The sea-ice cover has been reducing constantly for the past decade, and melting sea ice generates alkaline- or acidic-type melt-pond water, which dictates whether the melt-ponds behave as sources or sinks of atmospheric  $\text{CO}_2$  (Bates et al., 2014).

The Arctic contains large amounts of  $\text{CH}_4$ , mainly as methane hydrate in permafrost regions, sediments of outer continental margins, tundra, and wetlands (Kort et al., 2012; O'Connor et al., 2010). Emissions of  $\text{CH}_4$  from these sources are sensitive to climate change (Dlugokencky et al., 2011; Nisbet and Chappellaz, 2009), and have been reported during tundra freeze-in periods (Mastepanov et al., 2008), bubbling from thermokarst (or thaw) lakes (Walter et al., 2006), and leakage through the shallow East Siberian

Arctic shelf waters (Shakhova et al., 2010a, 2010b). For  $\text{N}_2\text{O}$ , soils and oceans are the dominant natural sources (Freitag et al., 2012), with the open ocean and coastal areas making up around 21% and 10% of the total atmospheric source of  $\text{N}_2\text{O}$  (Denman et al., 2007), respectively. On the other hand, agricultural and industrial activities are the main anthropogenic sources of  $\text{N}_2\text{O}$ . Melt water with low  $\text{CH}_4$  and  $\text{N}_2\text{O}$  is undersaturated, while under multiyear sea ice, the vicinity of the marginal ice zones, and the Mackenzie River plume, are oversaturated (Zhang et al., 2016). Zhang et al. (2016) suggested that frontal upwelling in the upper layer of the Arctic Ocean might contribute to atmospheric  $\text{CH}_4$  emissions, and reported water column and sedimentary sources of  $\text{CH}_4$  and  $\text{N}_2\text{O}$ . Kitidis et al. (2010) suggested that future sea-ice retreat might decrease the residence times of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  in the surface Arctic Ocean and enhance the sea-air flux of these greenhouse gases. The concentration of  $\text{N}_2\text{O}$  in the Canada Basin Intermediate Water (400–1500 m) is above preindustrial level, whereas it has remained at preindustrial level in the Canada Basin Deep Water (waters below 1500 m), suggesting that this water mass may be a preindustrial “relict” of  $\text{N}_2\text{O}$  (Zhan et al., 2015).

How is climate change going to affect sea-air greenhouse gas fluxes over the Arctic Ocean? Some studies show that ice-free conditions will allow the ocean to absorb more  $\text{CO}_2$  from the atmosphere (Bates and Mathis, 2009; Bates et al., 2006), but others show that the Arctic Ocean is unlikely to become a large sink of atmospheric  $\text{CO}_2$  (Cai et al., 2010; Mucci et al., 2010). Rapid atmospheric  $\text{CO}_2$  intrusion and low biological  $\text{CO}_2$  drawdown would result in a large increase of sea surface  $\text{CO}_2$  concentration across the Canada Basin, acting as a barrier for further  $\text{CO}_2$  influxes (Cai et al., 2010). Incubation experiments and continued flux monitoring are needed to improve our knowledge of  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$  net production and consumption rates. There is also a need to improve our knowledge of the relationship of  $\text{N}_2\text{O}$  with ice algae and the microbial community.

#### 4 Nutrient limitation and phytoplankton response

The availability of nutrients in seawater is important because biolimiting elements regulate oceanic primary production and the efficiency of the biological pump. Generally, nutrient-rich waters are mainly occupied by large phytoplankton (i.e., diatoms) (Zhuang et al., 2016). Silica-walled diatoms contribute considerably to the biological pump; they are efficient carbon carriers and food source, since they can sink rapidly and become available to the benthic fauna (Boyd and Newton, 1999). Zooplankton grazing and the microbial loop control microalgae (Jiao et al., 2010; Piepenburg, 2005). The nutrient response and the efficiency of the biological pump in the Arctic Ocean have become a central concern over

the last decades, because of their close link with the carbon cycle and global change. The biological pump may be affected by the extent of the sea ice and river runoff, which are, in turn, affected by the anthropogenic temperature increase (Anderson et al., 1998). Analysis of nitrate ( $\text{NO}_3^-$ ), phosphate ( $\text{PO}_4^{3-}$ ), silicate ( $\text{SiO}_3^{2-}$ ), and chlorophyll *a* concentrations (Bates et al., 2014), and *in situ* nutrient enrichment experiments have been conducted to assess the impact of macronutrient limitation on phytoplankton biomass and community structure in the western Canada Basin (Bates et al., 2014). Time-series experiments have also been conducted at an ice station in the central Arctic where fast ice was melting, allowing the determination of nutrient levels in fast-ice cores and in the ice–water interface (Zhuang et al., 2011). Calculation of diffusive fluxes of  $\text{SiO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ , and  $\text{NO}_3^-$  suggested that strong denitrification processes were occurring on the Chukchi Shelf (Zhang et al., 2015).

Concentrations of dissolved inorganic nitrogen (DIN) and  $\text{SiO}_3^{2-}$  in the upper layers of the Canada Basin are extremely low ( $0.31$  and  $0.94 \mu\text{mol}\cdot\text{L}^{-1}$ , respectively), with an N/P ratio of  $0.42$ , and an N/Si ratio of  $0.32$ . Such large deviations from the Redfield ratio indicate limitations in nitrogen and silica (Li et al., 2015). Concentrations of DIN in sea ice are approximately three to four times higher than in surface water, suggesting that the melting ice is delivering DIN to the surface water (Zhuang et al., 2011). Compared with nutrient-rich winter/early-spring Canada Basin shelf waters,  $\text{NO}_3^-$  (less than  $6 \mu\text{mol}\cdot\text{kg}^{-1}$ ) and  $\text{PO}_4^{3-}$  (less than  $1 \mu\text{mol}\cdot\text{kg}^{-1}$ ) are low in the sediments and the waters of the Chukchi Shelf (Bates et al., 2014). Strong denitrification processes in the sediments of the Chukchi shelf act as an important sink for  $\text{NO}_3^-$  (Zhang et al., 2015). In contrast,  $\text{SiO}_3^{2-}$  and dissolved oxygen concentrations are lower in deep Canada Basin water than in the remnant winter/early-spring water on the shelf and slope of the Chukchi Sea (this water lies below the mixed layer, which is at a depth of approximately  $15\text{--}25$  m; Bates et al., 2014). Higher nitrate and nitrite concentrations have been found in sea-ice cores, but higher  $\text{SiO}_3^{2-}$  and  $\text{PO}_4^{3-}$  concentrations were found in the surface seawater beneath the ice–water interface (Zhuang et al., 2011). Biogenic silica and chlorine content in marine surface sediments in the Chukchi Sea indicate two high production areas: one on the slope of the Chukchi Sea ( $72^\circ\text{N}$ ), and the other in the southern Chukchi Sea, where Anadyr Water (AW) and the Eastern Siberian Coastal Water meet ( $68^\circ\text{N}$ ). Low production areas are located in the eastern Chukchi Sea, which is under the influence of the Alaskan Coastal Water (ACW). The main factors controlling the distribution patterns of biogenic silica include upper primary productivity, circulation patterns in the Chukchi Sea (especially Pacific water inflow into the Chukchi Sea), and the influence of sea ice (Wang et al., 2015; Zhang et al., 2015).

Over the past decades, the Arctic basin has experienced ice-free conditions in the summer because of

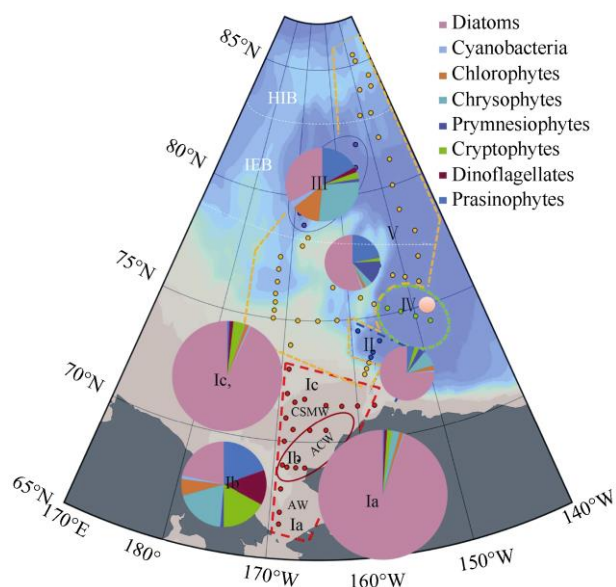
the shrinkage of the sea-ice cover. Studies conducted during CHINAREs-Arctic from 2008 to 2014 have recorded the effect of sea-ice retreat on several phytoplankton groups. Melting of summer sea ice reduces the thickness of the pack ice in the central Arctic, and the resulting freshwater leads to a dramatic salinity gradient and surface freshening under the ice (Steinacher et al., 2009). *In situ* observations, pigment analyses, and nutrient and phytoplankton observations at a fixed floating ice pack were conducted (Zhuang et al., 2017; Coupel et al., 2012) to examine the impact of sea-ice retreat on the distribution of dominant algae (Zhuang et al., 2017; Coupel et al., 2012), and on the biological pump (Coupel et al., 2012). The results imply that the freshening of the Arctic Ocean will have a negative impact on the phytoplankton community in the surface layer under the ice (Coupel et al., 2015), shifting it towards one dominated by chlorophytes in a future warm and fresh Arctic Ocean (Zhuang et al., 2017). This will ultimately reduce the biomass and production in the deep Arctic basin, as the freshening also deepens the nutricline (Coupel et al., 2015) and reinforces stratification, which would, in turn, reduce light and nutrient availability for phytoplankton growth (Coupel et al., 2012).

The Pacific inflow onto the Chukchi Shelf is one of the mechanisms through which the Arctic Ocean freshens. By determining nutrients, photosynthesis pigments, and size-fractionated chlorophyll *a*, Zhuang et al. (2016) found high levels of phytoplankton biomass on the shelf during summer, in response to the well-stratified water column and adequate nutrient supply from the Pacific Ocean, with large diatoms dominating the phytoplankton community. However, community structure in the eastern part of the shelf was altered by the nitrate-poor ACW, which promoted dinoflagellate and chrysophyte growth (Zhuang et al., 2016).

As phytoplankton are the first links in the marine food chain, the study of their composition, distribution, abundance, and biomass is of vital importance (Jin et al., 2017) (Figure 1). Tracking important changes in these parameters and linking them to the melting of sea ice and/or increase of freshwater input to the Arctic Ocean will allow us to determine the consequences of these changes, such as the possibility of northward migration of fishing grounds in response to phytoplankton changes.

## 5 Ocean acidification

The uptake of anthropogenic  $\text{CO}_2$  by the ocean decreases seawater pH and the saturation state of the carbonate mineral aragonite ( $\Omega_{\text{arag}}$ ), a process known as ocean acidification (Qi et al., 2017). The Arctic Ocean is expected to become undersaturated in aragonite ( $\Omega_{\text{arag}} < 1$ ) sooner than other oceans (Steinacher et al., 2009) because it is subject to several processes that can reduce pH and  $\Omega_{\text{arag}}$  and intensify  $\text{CO}_2$ -driven ocean acidification in high-latitude regions. These processes include: intrusion of



**Figure 1** Phytoplankton in the western Arctic Ocean during the summer of 2008. Stations were divided into five provinces based on physical and chemical properties (salinity, temperature, depth, nitrate and phosphate). These refer to: the Chukchi Shelf (province I, 66°N–73°N, red dots inside the red trapeze), the Border Zone (province II, from shelf to deep basin, 72°N–75°N, blue dots), the Mendeleev Abyssal Plain (province III, 78.8°N–82°N purple dots inside the purple circle), the South Canada Basin (province IV, 74°N–75.27°N, green dots inside the green circle), and the Shelf-slope-Canada Basin (province V, stations mainly north of 75°N, yellow dots inside the yellow geometrical figure). The pie charts show the mean relative proportion of the phytoplankton community by class level, and the size of the pie charts denote chlorophyll *a* biomass. A subdivision was made in province I (Ia, Ib, and Ic) due to differences in the dominant phytoplankton group: diatoms dominate in Ia and Ic, and pico- and nano-size algae dominate in Ib. The white dotted line and characters indicate ice cover conditions, separating the heavy-ice basin (HIB, ice coverage > 70%) from the ice-edge basin (IEB, 20% < ice coverage < 70%) (Coupel et al., 2012). The presence of three water masses is indicated inside the red trapeze: CSMW (Chukchi Shelf Modified Water), ACW (Alaskan Coastal Water), and AW (Atlantic Water) (Source: Jin et al., (2017)).

anthropogenic CO<sub>2</sub>, enhanced seasonal melting of sea ice (Yamamoto-Kawai et al., 2009a), respiration of organic matter (Bates and Mathis, 2009), upwelling along continental shelves (Mathis et al., 2012), and riverine inputs (Mathis et al., 2011). Additionally, reduction in the extent and duration of the Arctic and subarctic sea-ice cover indirectly provides a positive feedback to ocean acidification, as more open water allows for greater uptake of atmospheric CO<sub>2</sub> (Mathis et al., 2015). Reductions in sea-ice extent and thickness in the western Arctic Ocean have been especially pronounced in the Chukchi Sea and in the adjacent Canada Basin (Stroeve et al., 2007). Rapid loss of summer sea ice, along with increased input of melt water

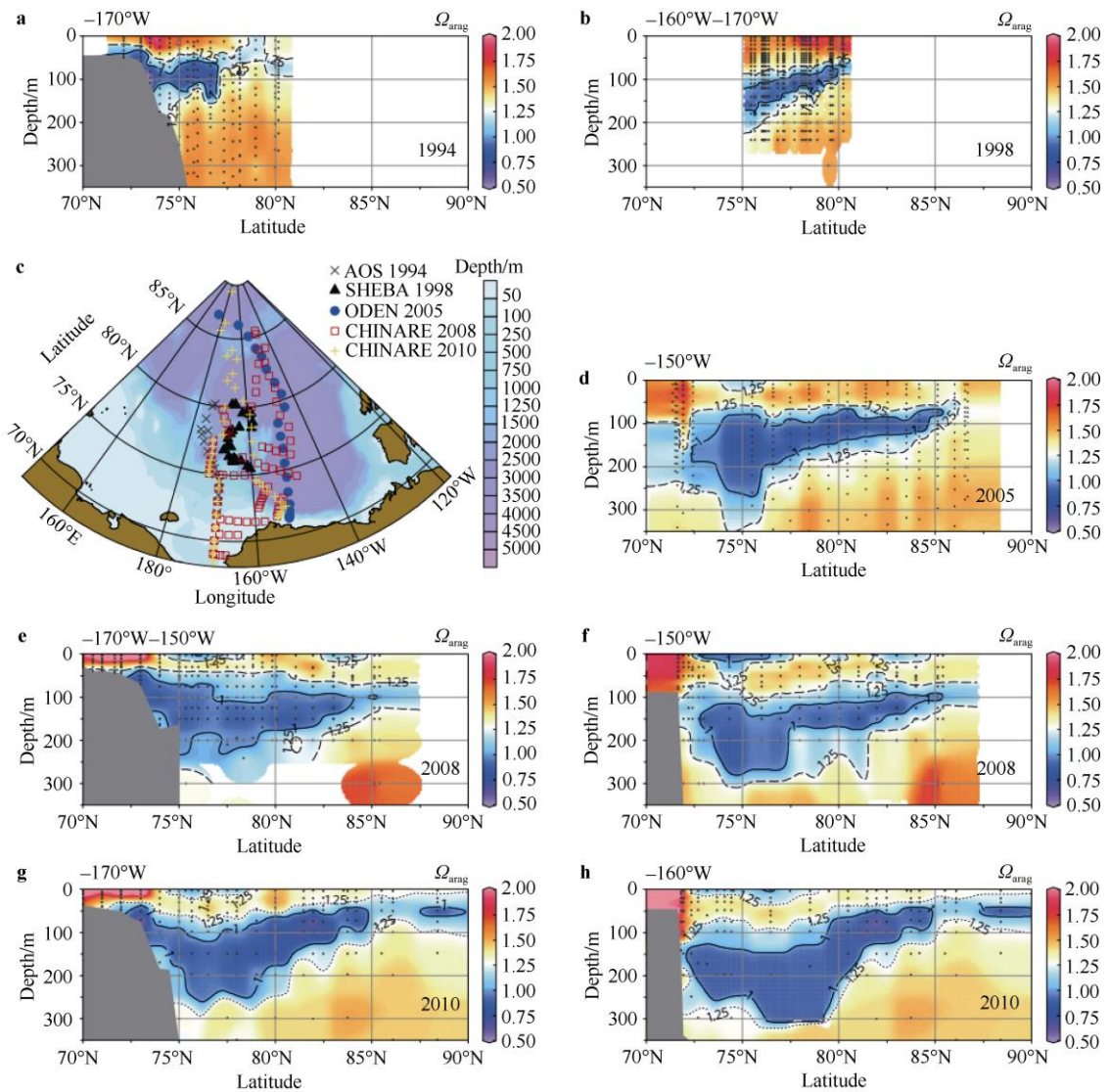
and freshwater, has deep implications for the biology and physio-biogeochemical conditions of the Arctic Ocean (Arrigo et al., 2008; McGuire et al., 2009, 2006; Pabi et al., 2008). Melting of sea ice has freshened the surface water throughout this area (Yamamoto-Kawai et al., 2009b), lowering  $\Omega_{\text{arag}}$  and producing corrosive conditions in surface waters in some areas (Bates et al., 2014; Mathis et al., 2011; Yamamoto-Kawai et al., 2009a). Halocline waters formed on the Chukchi Shelf, exported to the deep Arctic Ocean (Mathis et al., 2007), and upwelled on the Canada Basin, are the primary natural process contributing to corrosive events in the Beaufort Sea (Mathis et al., 2012). The deep Makarov and Canada basins also receive highly calcium carbonate corrosive waters (at a depth range of 50–150 m) produced along the bottoms of the East Siberian seas. The signature of this subsurface water is kept within the Beaufort Gyre, and is exported out to the North Atlantic through the eastern Fram Strait, and likely also through the Canadian Arctic Archipelago (Anderson et al., 2017).

Aragonite undersaturation gradually progresses upstream as the waters move north from the Pacific Ocean through each of the three continental shelf seas in the Pacific Arctic region (the Beaufort, Chukchi, and Bering seas). This is why each sea is expected to become undersaturated progressively at approximately 30-year intervals (Mathis et al., 2015). The annual mean for  $\Omega_{\text{arag}}$  is expected to pass below the current range of natural variability in 2025 for the Beaufort Sea, 2027 for the Chukchi Sea, and 2044 for the Bering Sea. Undersaturation is expected to arrive later in the Bering Sea because of the higher range of natural variability of  $\Omega_{\text{arag}}$  that occurs here (Mathis et al., 2015). Some shelf waters and deep waters in the Canada Basin have  $\Omega_{\text{arag}}$  and calcite saturation state values of approximately 0.5 to 4.0. Calcite saturation state values of less than one have been measured, indicating that these waters are potentially corrosive for calcite (Bates et al., 2014). Moreover, between the 1990s and 2010, waters with low  $\Omega_{\text{arag}}$  expanded northwards to 85°N, and deepened to 250 m, covering 5% to 31% of the total area north of 70°N (Qi et al., 2017) (Figure 2). The expansion and deepening are primarily caused by air–sea CO<sub>2</sub> exchange, melting of sea ice, and increased Pacific Winter Water transport driven by an anomalous circulation pattern and sea-ice retreat. Local carbon recycling and anthropogenic CO<sub>2</sub> uptake have also contributed to this phenomenon (Qi et al., 2017). These results indicate that acidification is occurring more rapidly in the Arctic Ocean than in the Pacific and Atlantic oceans, with the western Arctic Ocean being the first open-ocean region where large-scale expansion of acidified water has been directly observed in the upper water column (Qi et al., 2017).

## 6 Organic carbon export and burial

Organic carbon export and burial data are important to evaluate the Arctic Ocean's response to climate change.



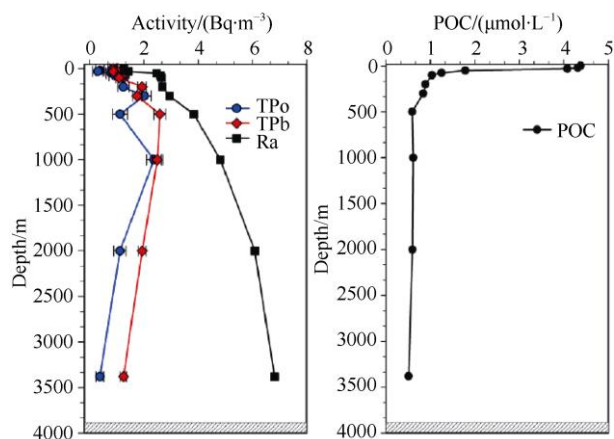


**Figure 2** Latitudinal distribution of aragonite mineral saturation state ( $\Omega_{\text{arag}}$ ), showing the expansion of acidifying water in the western Arctic Ocean. Data is from different cruises from 1994 to 2010. **a**, Arctic Ocean Section 1994 (AOS 1994). **b**, Surface Heat Budget of the Arctic Ocean 1998 (SHEBA 1998). **c**, Station map of all cruises with the color bar showing water depths. **d**,  $\Omega_{\text{arag}}$  for Beringia 2005 (ODEN 2005). **e-h**,  $\Omega_{\text{arag}}$  for CHINARE-Arctic 2008 and CHINARE-Arctic 2010 (Source: Qi et al., 2017).

Isotope tracers have been used as powerful tools to study particle dynamics and to trace the export flux of organic carbon from the euphotic layer to the deep sea. Chen et al. (2012) used the  $^{234}\text{Th}/^{238}\text{U}$  disequilibria to estimate scavenging fluxes of  $^{210}\text{Pb}$  from the water column to the underlying sediments in the Chukchi Sea, showing that  $^{210}\text{Pb}$  lateral transport fluxes ranged from 17 to 177  $\text{Bq}\cdot\text{m}^{-2}\cdot\text{a}^{-1}$ , constituting 63%–94% of the total supply of  $^{210}\text{Pb}$  in the eastern Chukchi Sea. They also found an unusual  $^{210}\text{Po}/^{210}\text{Pb}$  disequilibrium in the deep water of the Bering Basin, which indicated an enhanced particle scavenging that was unique in global deep seas (Hu et al., 2014) (Figure 3).

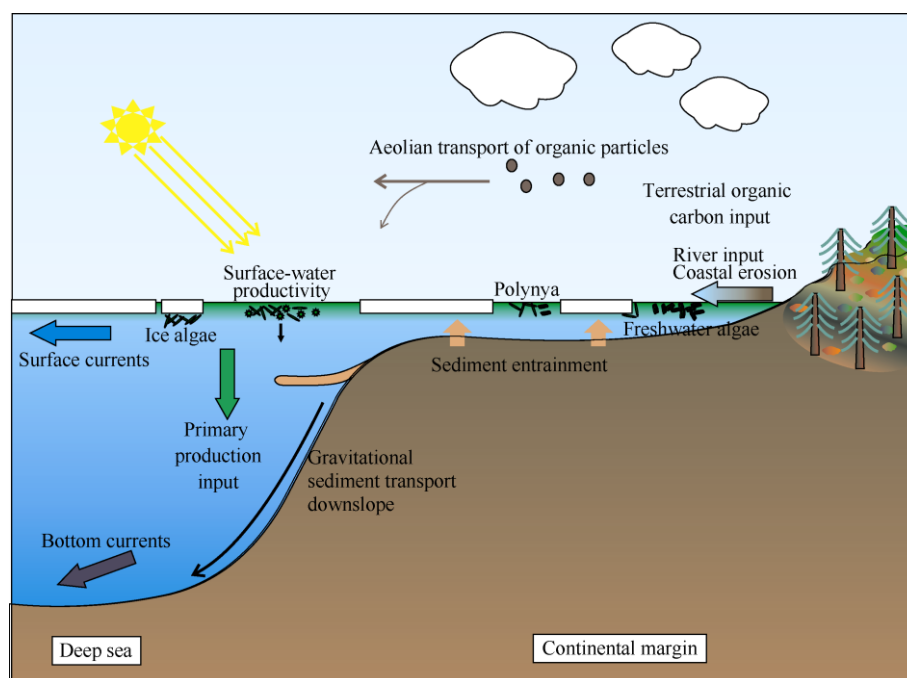
Organic carbon buried in marine sediments acts as a net sink of atmospheric  $\text{CO}_2$ , which would help decrease  $\text{CO}_2$  levels in the atmosphere (Chen et al., 2015).

Permafrost around the Arctic Ocean contains about half of the global soil organic carbon. Changes in the Arctic region have enhanced both the transport of organic carbon that has been stored in permafrost to the ocean, and the role of the biological pump in the water column of the Arctic Ocean (Chen et al., 2015, 2004; Liu et al., 2011; Li et al., 2008, 2007). Organic carbon from terrigenous sources has a different chemical composition from the one in the biological pump. To fully understand eutrophication, increase in oxygen minimum zones, and other processes occurring in the Arctic Ocean, it is important to find out more about organic carbon in the sediments of the Arctic Ocean: its sources, burial processes, and feedback to climate change (Stein and MacDonald, 2004) (Figure 4).



**Figure 3** Total  $^{210}\text{Po}$ ,  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$ , and particulate organic carbon (POC) profiles in the Aleutian Basin adjacent to the Bering shelf. The  $^{210}\text{Po}/^{210}\text{Pb}$  disequilibrium in the deep basin suggested enhanced particle scavenging in the deep water (Source: Hu et al., 2014).

Biomarkers have been widely used to trace the sources and burial processes of organic carbon in the Arctic Ocean (Feng et al., 2015a, 2015b, 2013). Biomarkers for organic matter in surface sediments and seawater include brassicasterol, dinosterol, and long chain alkenones. Brassicasterol is frequently used as a biomarker for marine algal matter, especially diatoms (Volkman, 1986). Dinosterol is commonly used as a biomarker for organic matter derived from dinoflagellates in sediments and seawater, although it has also been found in prymnesiophytes of the genus *Pavlova* (Volkman et al., 1990) and in the diatom *Navicula speciosa*, especially in marine sediments lacking contributions of organic matter from dinoflagellates (Volkman et al., 1993). Alkenones with 37 to 39 carbon atoms and 2–4 double bonds are used to trace a few phytoplankton species of the class Prymnesiophyceae (Marlowe et al., 1984) (Figure 5).

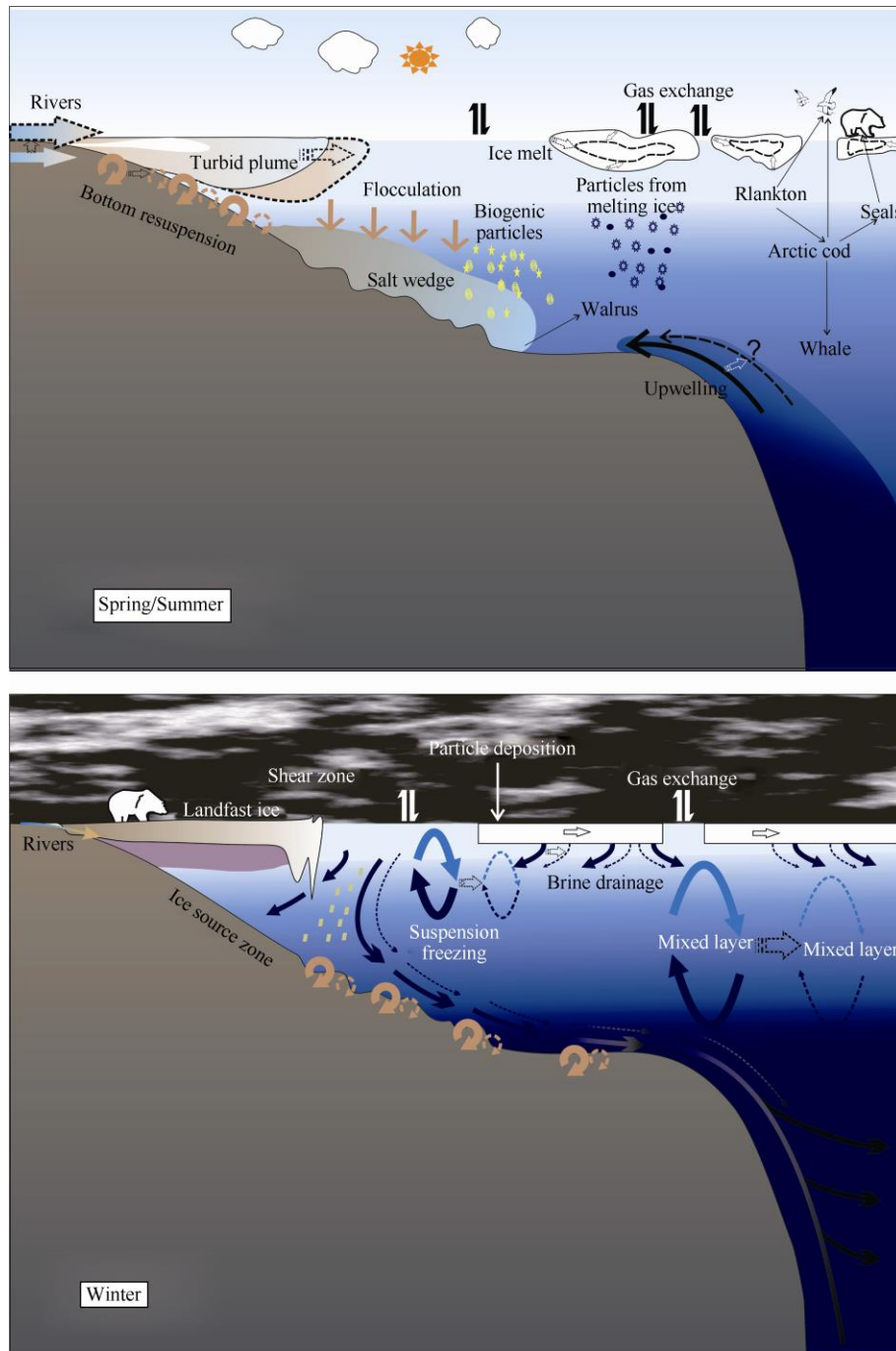


**Figure 4** Schematic diagram showing input of organic carbon into the Arctic Ocean (modified from Stein and Korolev, 1994).

Lipids have also been used to trace the sources of organic carbon in the Arctic Ocean. During the second CHINARE-Arctic in the western Chukchi Sea in 2003, lipids were extracted from surface sediments (Bai et al., 2010b). Total concentrations of lipids (brassicasterol, dinosterol, and alkenones combined) were between 20 and 3149  $\text{ng}\cdot\text{g}^{-1}$  lipid weight, with an average value of 1010  $\text{ng}\cdot\text{g}^{-1}$  lipid weight. Lipid concentration indicated that primary productivity on the Chukchi Shelf was higher than that on the Chukchi plateau. Ratios of brassicasterol to dinosterol varied, but brassicasterol was the predominant lipid at all sampling stations. On the Chukchi Shelf, diatoms

were the main phytoplankton group. Brassicasterol and dinosterol accounted for 42%–74% and 17%–37% of the total lipid biomarkers, respectively. On the plateau, diatoms were the dominant phytoplankton group. In the Canada Basin, coccolithophore was dominant, while diatoms were the minority. Lignin is only produced by vascular plants, and has been widely used to trace the percentage of terrigenous organic carbon in the marine environment. Xu et al. (2017) and Wang et al. (2017) detected lignin in surface sediments from the Bering and Chukchi seas. Woody gymnosperms were predominant at the easternmost stations located in the northern Bering Sea, while refractory





**Figure 5** Changes in biogeochemical processes in the Arctic Ocean under global warming (modified from Stein and MacDonald, 2004). Solid lines indicate original processes in the Arctic Ocean, and dotted lines indicate processes taking place under global warming.

non-woody angiosperm and fresher gymnosperm tissues were predominant at the stations in the Chukchi Sea, and a signal of fresher woody gymnosperm tissues was found at the northernmost stations located in the Chukchi Sea. The fresher materials found in the northernmost Chukchi Sea could have been transported here via ice-rafting processes. Detection of fresh lignin materials and the occurrence of lignin decomposition mean that this region could be sensitive to the impact of climate change.

Biomarkers have also been widely used to trace the burial process of organic carbon in the Arctic Ocean. Extracted lipids from sediments of the Chukchi Sea were used to reconstruct primary production. Bai et al. (2010a) showed an increase in total and individual primary productivity over the last 500 years. The phytoplankton community structure mostly showed a decrease in coccolithophorids, an increase in diatoms, and no obvious changes in the relative abundance of dinoflagellates. This

may be related to the nutrient structure in the Chukchi Sea, which is determined by the waters from the North Pacific Ocean and the change in the summer sea-ice cover in the Chukchi Sea. Xiao et al. (2017) presented a sea-ice record back to 15 cal. ka BP (calendar kilo years before present) based on the sea-ice biomarker IP<sub>25</sub>, the phytoplankton biomarker brassicasterol, and a terrigenous biomarker of long-chain *n*-alkanols from the piston core MD99-2272 obtained in the North Icelandic shelf. During the Bølling/Allerød (14.7–12.9 ka), the North Icelandic shelf was characterized by extensive spring sea-ice cover linked to reduced flow of warm Atlantic Water and dominant Polar water influence, as well as strong melt water input in the area. This pattern showed an anti-phase relationship with the ice-free/less ice conditions in marginal areas of the eastern Nordic Seas, where the Atlantic Water inflow was strong, and contributed to an enhanced deep-water formation. Prolonged sea-ice cover with occasional occurrence of seasonal sea ice prevailed during the Younger Dryas (12.9–11.7 ka) interrupted by a brief interval of enhanced Irminger Current and deposition of the Vedde Ash, as opposed to abruptly increased sea-ice conditions in the eastern Nordic Seas. The seasonal sea ice decreased gradually from the Younger Dryas to the onset of the Holocene corresponding to increasing insolation. Ice-free conditions and sea surface warming were observed for the Early Holocene, followed by expansion of sea ice during the Mid-Holocene.

## 7 Future work of Chinese Arctic biogeochemistry studies

There has been tremendous progress in the study of the Arctic Ocean biogeochemistry over the past decades. This Ocean is undergoing rapid changes in its physical, chemical, and biological characteristics that will lead to shifts in ecosystem regimes, variations in the rate of carbon burial and the efficiency of the biological pump, and may also trigger ocean acidification and other environmental consequences, yet unknown. Some of the future aspects of Chinese biogeochemistry studies in the Arctic Ocean may include, but are not limited to, the following:

(1) The physical, biological, and microbial carbon pumps determine the carbon budget. For example: increased seawater temperature decreases CO<sub>2</sub> solubility, and increased flux of warm and fresh water weakens the physical pump. Can these changes counteract the effects of an enhanced biological pump in the Arctic Ocean under global warming?

(2) The Arctic Ocean is a sink of atmospheric CO<sub>2</sub>. Arctic warming is also causing rapid changes in terrestrial ecosystems, thawing of permafrost, and enhanced weathering in drainage basins. These changes will, in turn, release additional CO<sub>2</sub> into the atmosphere. Can an enhanced biological pump counteract the emissions of CH<sub>4</sub>

and CO<sub>2</sub> from the permafrost around the Arctic Ocean?

(3) How will variations of Pacific inflow, Atlantic water exchange, melting of sea ice, and river discharge affect greenhouse gas budgets, nutrient dynamics, nitrogen fixation, and denitrification?

(4) What is the impact of global warming on sedimentary organic carbon in the Arctic Ocean? Global warming will enhance the biological pump and increase input of terrigenous organic carbon into the Arctic Ocean. The composition of organic carbon in this Ocean is heterogeneous and very complicated. How can we identify the signals of organic carbon from the biological pump and terrigenous sources separately, enabling us to track changes and forcings through geological time?

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