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The Arctic Ocean marine carbon cycle: evaluation of air-sea CO_2 exchanges, ocean acidification impacts and potential feedbacks

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Abstract

At present, although seasonal sea-ice cover mitigates atmosphere-ocean gas exchange, the Arctic Ocean takes up carbon dioxide (CO_2) on the order of −65 to −175 Tg C year^{-1}, contributing 5–14% to the global balance of CO_2 sinks and sources.
Because of this, the Arctic Ocean is an important influence on the global carbon cycle, with the marine carbon cycle and atmosphere-ocean CO_2 exchanges sensitive to Arctic Ocean and global climate change feedbacks. In the near-term, further sea-ice loss and increases in phytoplankton growth rates are expected to increase the uptake of CO_2 by Arctic surface waters, although mitigated somewhat by surface warming in the Arctic. Thus, the capacity of the Arctic Ocean to uptake CO_2 is expected to alter in response to environmental changes driven largely by climate. These changes are likely to continue to modify the physics, biogeochemistry, and ecology of the Arctic Ocean in ways that are not yet fully understood. In surface waters, sea-ice melt, river runoff, cooling and uptake of CO_2 through air-sea gas exchange combine to decrease the calcium carbonate ($CaCO_3$) mineral saturation states (Ω) of seawater that is counteracted by seasonal phytoplankton primary production (PP). Biological processes drive divergent trajectories for Ω in surface and subsurface waters of Arctic shelves with subsurface water experiencing undersaturation with respect to aragonite and calcite. Thus, in response to increased sea-ice loss, warming and enhanced phytoplankton PP, the benthic ecosystem of the Arctic shelves are expected to be negatively impacted by the biological amplification of ocean acidification. This in turn reduces the ability of many species to produce $CaCO_3$ shells or tests with profound implications for Arctic marine ecosystems.

1 Introduction

The Arctic Ocean is currently experiencing rapid environmental change due to natural and anthropogenic factors that include warming (e.g., Serreze et al., 2000; Polyakov et

al., 2002; Serreze and Francis, 2006; Overland et al., 2008), sea-ice loss (Cavalieri et al., 2003; Maslanik et al., 2007; Giles et al., 2008; Comiso et al., 2008), and other physical changes (Wu et al., 2005; McGuire et al., 2006) as well as biology and ecosystem structure changes (Arrigo et al., 2008; Pabi et al., 2008). These changes and feedbacks could have profound impacts on the Arctic Ocean marine carbon cycle and the importance of the Arctic for the global carbon cycle and the balance of carbon dioxide (CO_2) sinks and sources. In a recent review, Macdonald et al. (2009) compiled inorganic and organic carbon budgets of the Arctic Ocean. Here, we review the present understanding of the marine inorganic carbon cycle, air-sea CO_2 disequilibrium and rates of air-sea CO_2 gas exchange, the physical and biological processes that influence Arctic Ocean CO_2 sinks and sources, the impact of ocean acidification and the potential future drivers of change such as sea-ice loss, phytoplankton primary production (PP) and freshwater inputs. The geographic scope of this review encompasses the Arctic Ocean shelves (i.e., Barents, Kara, Laptev, East Siberian, Chukchi, Beaufort and Canadian Archipelago Seas) and central basin (i.e., Canada and Eurasian Basin), but does not extend to the gateways of the Arctic Ocean including the Greenland, Icelandic, Norwegian, and Bering Seas, and Hudson and Baffin Bays.

As context for this paper, a brief background on the physical and biogeochemical setting is presented in Sect. 2. Relevant information about historical sampling in the Arctic Ocean, methods for estimating air-sea CO_2 exchange rates, considerations about carbonate chemistry and relationships between shelf metabolism (net autotrophy versus net heterotrophy) and CO_2 sink/source issues are summarized in Sect. 3. With a synthesis of published results and data, the present status and magnitude of the Arctic Ocean CO_2 sink on the Arctic shelves and central basin is estimated, with predictions for near-term CO_2 flux rates in an era of rapid change (Sect. 4). The impacts of rapid change in the Arctic and the potential feedbacks on the marine inorganic carbon cycle and air-sea CO_2 exchange rate are also discussed in Sect. 5. Vulnerabilities of the Arctic marine carbon cycle relate to such factors as sea-ice loss and warming, biological and ecosystem changes, and hydrological/freshwater input changes. We also discuss

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the impact of ocean acidification, and biology and physical processes on the marine carbon cycle and calcium carbonate ($CaCO_3$) mineral saturation states in the Arctic (Sect. 6).

2 The physical and biological setting of the Arctic Ocean

There are multiple influences on the marine carbon cycle and air-sea exchange of CO_2 in the Arctic Ocean. The inorganic carbon cycle is dominated by inter-ocean exchanges between the Pacific and Atlantic Oceans (Macdonald et al., 2009) and subsequent biogeochemical modifications and transformations of water while resident in the Arctic during transit between these oceans. In addition, river inputs of freshwater and materials, sea-ice production and melting, and atmosphere-ocean interaction and exchanges also have profound influence.

The relatively small Arctic Ocean ($\sim 10.7 \times 10^6$ km^2) is almost completely landlocked except for the Bering Strait, Canadian Archipelago, Fram Strait and Norwegian Sea gateways that allow exchanges with the Pacific and Atlantic Oceans (Fig. 1). The relatively broad, generally shallow (<200 m deep) and almost annular continental shelves surrounding the central basin comprise about 53% of the area of the Arctic Ocean, making it unique compared to other ocean basins. All of the Arctic continental shelves are highly varied, unique and difficult to characterize generically.

As a framework for this review, the Chukchi and Barents Seas can be characterized as "inflow" shelves (Carmack and Wassmann, 2006) where the import of nutrient-rich water from the Pacific and Atlantic Oceans, respectively, sustains high rates of seasonal phytoplankton PP or net community production (NCP). Other shelves such as the Kara, Laptev, East Siberian and Beaufort Seas constitute "interior shelves", which are highly influenced by exchanges with other shelves, while the Canadian Archipelago represents an "outflow shelf" where Arctic water is exported to the Atlantic Ocean via Hudson and Baffin Bays. In the central basin of the Arctic Ocean, waters of the Canada Basin or Beaufort Gyre are separated from the Eurasian Basin by the surface trans-

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polar drift, with inputs and outputs of Atlantic Ocean water through the Fram Strait and shelf-basin exchanges of water across the entire Arctic. Central basin waters are highly stratified vertically with distinct different physical and chemical properties of surface waters and subsurface halocline, Atlantic layer and deep-water layers, with deep waters having limited exchanges with the Atlantic Ocean.

The Arctic Ocean has an important role in the global freshwater cycle (e.g., Aagaard and Carmack, 1989; Wijffels et al., 1992; Woodgate and Aagaard, 2005) and Atlantic Ocean overturning circulation (e.g., Walsh and Chapman, 1990; Mysak et al., 1990; Hakkinen, 1993; Aagaard and Carmack, 1994; Wadley and Bigg, 2002). Surrounding the Arctic Ocean is an extensive land margin and watershed that contributes freshwater and material inputs such as inorganic nutrients and dissolved organic carbon (DOC) to the Arctic Ocean (Opsahl et al., 1999; Dittmar and Kattner, 2003; Benner et al., 2003; Guo et al., 2004). Siberian (Ob, Yenisey, Lena and Kolyma) and North American (Mackenzie, Yukon) rivers contribute significantly to land-ocean inputs (Peterson et al., 2002; McGuire et al., 2006; Serreze et al., 2006; Cooper et al., 2008). Finally, air-sea interaction controls the seasonal sea-ice advance and retreat, and interannual changes of sea-ice distributions and thickness, and sea-ice export from the Arctic Ocean (Carmack and Chapman, 2003). In wintertime, the Arctic is completely covered by sea-ice (except for polynyas and leads) with thick (3–7 m) multi-year ice occupying the interior of the central basin and thinner seasonal sea-ice (1–2 m) across the Arctic shelves and periphery (e.g., significant parts of the Bering Sea shelf; Hudson and Baffin Bays; Greenland, Iceland and Norwegian Sea) that melts and retreats towards the Pole during the summertime. While the seasonal production and melting of sea-ice contributes significantly to the physical structure and mixing of the Arctic, sea-ice melt and brine rejection during sea-ice formation also modifies the biogeochemical properties of surface and halocline layers (Steele and Boyd, 1998; Weingartner et al., 1998; Carmack and Chapman, 2003). The Arctic Ocean sea-ice cover is also particularly sensitive to interannual changes and variability of atmosphere-ocean-sea-ice forcing and feedbacks associated with climate variability such as the Arctic Oscillation (AO) and Arctic

Sea-Ice Oscillation (ASIO) (e.g., Rigor et al., 2002; Overland and Wang, 2005; Wang et al., 2005).

3 Considerations about sampling, carbonate chemistry, air-sea CO_2 exchange calculations and continental shelf CO_2 sink-sources issues

3.1 Marine inorganic carbon cycle sampling in the Arctic Ocean

Compared to many other open-ocean and coastal environments, relatively few studies of the marine inorganic carbon cycle and air-sea CO_2 exchange rates have been conducted in the Arctic. The harsh polar climate and difficult logistical support have limited most studies to opportunistic icebreaker surveys conducted on the Arctic shelves during the summertime sea-ice retreat with a couple of transpolar surveys across the deep basin (e.g., Arctic Ocean Section; Tucker and Cate, 1996; Anderson et al., 1998a; Jutterstrom and Anderson, 2005; Jones et al., 2008; Tanhua et al., 2009; Carbon in the North Atlantic (CARINA) datasets at http://cdiac.ornl.gov/). The absence of long-term ocean time-series (e.g., Winn et al., 1994; Bates, 2007; Santana-Casiano et al., 2007), repeat hydrographic surveys (e.g., Sabine et al., 2004; Feely et al., 2004) and underway shipboard surface observations (Takahashi et al., 2002, 2009) that have benefited understanding of seasonal and interannual change in other ocean basins and coastal ocean environments has considerably constrained our knowledge of the marine carbon cycle, and CO_2 sink and source terms in the Arctic Ocean.

3.2 Carbonate chemistry considerations

Studies of the marine inorganic carbon cycle in the Arctic have focused on measurements of one or more of the four directly observable carbonate system parameters, that is either dissolved inorganic carbon (DIC), total alkalinity (TA), partial pressure of CO_2 (pCO_2), or pH. Early historical data of TA and pH were collected in the Arctic

(Yamamoto-Kawai et al., 2005) but have relatively limited use today due to inherent uncertainties associated with the analytical techniques used. More recently, improvement of analytical techniques, the advent of standardized methods (Dickson and Goyet, 1994; Dickson et al., 2007) and use of seawater standards and calibration have allowed precise and accurate data to be collected in the Arctic Ocean, and subsequently used for assessments of stocks, distributions and transformations of the marine inorganic carbon cycle.

Seawater carbonate chemistry is governed by a series of reactions, such that:

$$CO_{2\,(atmos)} \rightleftarrows CO_{2\,(aq)} + H_2CO_3 \rightleftarrows H^+ + HCO_3^- \rightleftarrows 2H^+ + CO_3^{-2} \tag{R1}$$

The four directly measureable carbonate system parameters are DIC, TA, pCO$_2$, and pH. For example, DIC is defined as (Dickson and Goyet, 1994; Dickson et al., 2007):

$$DIC = [CO_2^*] + [HCO_3^-] + [CO_3^{2-}] \tag{R2}$$

where $[CO_2^*]$ represents the concentration of all unionized carbon dioxide, present either as H_2CO_3 or as CO_2. The TA of seawater is defined as:

$$\begin{aligned}TA = {} &[HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] \\ &+[HS^-] + [NH_3] + [\text{minor species}] -[H^+]-[HSO_4^-]-[HF]-[H_3PO_4]- [\text{minor species}]\end{aligned} \tag{R3}$$

where $[HCO_3^-] + 2[CO_3^{2-}] + B(OH)_4^-$ are the primary components of seawater TA. Other species have minor contribution to TA. DIC and TA are expressed as μmoles kg^{-1}, pCO$_2$ is expressed as μatm, while pH is negative log of the $[H^+]$ activity generally expressed on the total seawater pH scale.

The complete seawater carbonic acid system (i.e., $[CO_2^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[H^+]$ and CaCO$_3$ mineral saturation states, Ω) can be calculated from a combination of two measured carbonate system parameters (i.e., DIC, TA, pCO$_2$ and pH). In this paper, we used the thermodynamic model of Zeebe and Wolf-Gladrow (2001), temperature and salinity data, the CO$_2$ solubility equations of Weiss (1974), and dissociation constants for carbonic acid (i.e., pK$_1$ and pK$_2$) of Mehrbach et al. (1973; as refit by Dickson

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and Millero, 1997), borate (Dickson, 1990) and phosphate (Dickson and Goyet, 1994). It should be noted that the experimental determinations of carbonic acid dissociation constants (i.e., Mehrbach et al., 1973; Goyet and Poisson, 1989; Roy et al., 1993) have lower limits of $-1°$C or $0°$C, and that the equations governing pK$_1$ and pK$_2$ have to be linearly extrapolated for seawater with temperatures less than $-0°$C. The difference in calculated seawater pCO$_2$ for different pK$_1$ and pK$_2$ determinations is relatively small ($<5\,\mu$atm) at temperatures less than $0°$C (Bates, 2006).

CaCO$_3$ mineral production and dissolution is governed by the following chemical reaction:

$$CaCO_3 = [Ca^{2+}] + [CO_3^{2-}] \tag{R4}$$

The CaCO$_3$ mineral saturation state (Ω) is defined as the ion product of carbonate and calcium concentrations, thus:

$$\Omega_{\text{aragonite}} = [Ca^{2+}][CO_3^{2-}]/K_{sp}^* \tag{R5}$$

The experimental solubility product (i.e., K_{sp}^*) of Mucci (1983) was used here. In general, CaCO$_3$ production and dissolution rates vary as a function of saturation state for aragonite ($\Omega_{\text{aragonite}}$) or calcite ($\Omega_{\text{calcite}}$). For example, dissolution is generally favored when $\Omega_{\text{aragonite}}$ values are lower than 1, while aragonite formation generally occurs at $\Omega_{\text{aragonite}}$ values greater than 1.

3.3 Air-sea CO$_2$ exchange rate considerations

Different approaches have also been used to estimate rates of air-sea CO$_2$ exchange for the Arctic shelves or entire Arctic Ocean. These approaches include: (1) differences in atmospheric and seawater pCO$_2$ (either by direct measurements of pCO$_2$ or calculated from other carbonate parameters) that gives ΔpCO$_2$ or air-sea CO$_2$ disequilibrium and, direction of air-sea CO$_2$ gas exchange (Olsen et al., 2003; Omar et al., 2007; Bates et al., 2006); (2) carbon mass balance assessments (e.g., Anderson et al., 1998; Fransson et al., 2001; Kaltin and Anderson, 2005; Macdonald et al., 2009); and;

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(3) direct measurements of air-sea CO_2 exchange through eddy correlation techniques (Semiletov et al., 2006).

In the first approach, $\Delta p CO_2$ data combined with knowledge of gas transfer velocities commonly parameterized as a function of contemporaneous windspeed data (e.g., Wanninkhof, 1992; Wanninkhof and McGillis, 1999) provide estimates of air-sea CO_2 exchange rates. If surface water $p CO_2$ values are undersaturated with respect to the atmosphere, $\Delta p CO_2$ values are negative and the ocean has the potential to uptake CO_2 (i.e., sink of CO_2) with the magnitude of exchange set by gas transfer velocities. If surface water $p CO_2$ values are oversaturated with respect to the atmosphere, $\Delta p CO_2$ values are positive and the ocean has the potential to release CO_2 to the atmosphere (i.e., source of CO_2).

In the second approach, air-sea CO_2 exchange rates can be calculated by mass balance assessment of carbon stocks and inputs/outputs of carbon (both inorganic and organic), or temporal/depth changes of DIC that account for temperature and salinity variability and such processes as phytoplankton PP and respiration, vertical entrainment/detrainment and vertical diffusion. Both approaches have considerable uncertainties with caveats and assumptions used in the approaches. The third approach, using eddy correlation techniques, has only been used once in the Arctic Ocean (Semiletov et al., 2007). The results of these different approaches are discussed in more detail in Sect. 4 for individual shelves and the central basin of the Arctic Ocean.

3.4 Continental shelf net metabolism and CO_2 sink-sources issues

The CO_2 source or sink status and net metabolism of the coastal ocean has been highly debated over the last few decades. In early papers, it was first suggested that continental shelves sequestered significant amounts of CO_2 and that the global coastal ocean was net autotrophic (i.e., net consumption of CO_2) and a significant sink for atmospheric CO_2 (Walsh et al., 1985; Walsh, 1991). Smith and Hollibaugh (1993) subsequently argued that the nearshore coastal ocean was net heterotrophic (i.e., net production of CO_2) and offshore shelf coastal ocean neutral, and thus continen-

tal shelves were potential sources of CO_2 to the atmosphere. Other studies have since suggested that the CO_2 source or sink status (Borges, 2005; Borges et al., 2005), and the metabolic status of continental shelves (i.e., net autotrophy versus net heterotrophy) is highly variable in time and space (e.g., Wollast, 1998; Gattuso et al., 1998).

The net metabolism (either net autotrophy or heterotrophy) of a continental shelf is influenced by a balance of transports, transformation and exchanges, such as: the input of organic matter (OM) from terrestrial sources, OM production and respiration in the coastal ocean, retention or export of OM from the shelf and, the net air-sea exchange of CO_2. The balance of these processes dictates the metabolic status (i.e., net autotrophic or heterotrophic), but can also influence the potential CO_2 sink or source status of the continental shelf in question. The spatial and temporal variability of seawater $p CO_2$ on continental shelves is acted upon by a complex interplay of connected and quasi-independent physical and biological factors. For example, the physicochemical process of air-sea CO_2 exchange can proceed independently of the biological processes (e.g., production versus consumption of OM) that dictate the metabolism of the coastal ocean. The variability of $p CO_2$ or $\Delta p CO_2$ and separation of biological and physical processes can lead, for example, to a net heterotrophic continental shelf still being a sink for atmospheric CO_2 (Ducklow and McAllister, 2005). Ducklow and McAllister (2005) suggested that the global coastal ocean was net autotrophic, and thus a potential sink for atmospheric CO_2.

Recent syntheses of coastal carbon cycle studies by Chen and Borges (2009) suggest that in general high-latitude and temperate continental shelf seas tend to be net annual sinks of atmospheric CO_2, while upwelling dominated, and subtropical to tropical coastal environments tend to release CO_2 to the atmosphere. In addition, localized shallow nearshore and river influenced areas of the continental shelves tend to be sources of CO_2 to the atmosphere, while the deeper, more expansive areas of the continental shelves tend to be oceanic sinks for atmospheric CO_2 (Chen and Borges, 2009). In summary, Chen and Borges (2009) suggest that the polar continental shelves, for example, are likely to be potential sinks for atmospheric CO_2. However,

this potential is also influenced by seasonal sea-ice cover, which act as a barrier to air-sea CO_2 gas exchange compared to open water conditions (Bates, 2006). Whether sea-ice facilitates the uptake or release of CO_2 is an area of active research with no definitive answer (Gosink et al., 1978; Semiletov et al., 2004; Delille et al., 2007). An additional complication is the recent finding that anaerobic microbial production of, and subsequent release of alkalinity can act to decrease seawater pCO_2, which in turn may enhance the uptake of atmospheric CO_2 onto continental shelves where sediments significantly interact with surface waters (Thomas et al., 2009).

4   Present state of knowledge about the marine inorganic carbon cycle and air-sea CO_2 exchange rates of the Arctic Ocean

4.1   Arctic ocean shelves: inflow shelves

4.1.1   Barents sea shelf

The Barents Sea comprises a broad and shallow continental shelf that is dominated by inflowing Atlantic water with minimal freshwater inputs. In the Barents Sea, warm and salty surface Atlantic Ocean water inflows from the Norwegian Sea into the Barents Sea via the Norwegian Atlantic Current (Skelvan et al., 1999, 2005; Omar et al., 2007), with ~2 Sv exchange between the Atlantic and Barents Sea (Gammelsrod et al., 2008). Cooling of surface water and brine rejection during sea-ice formation is subsequently thought to transform this surface water into dense subsurface water that is subsequently exported to the Kara Sea and central basin of the Arctic Ocean (Anderson et al., 1994; Fransson et al., 2001; Kaltin et al., 2002; Omar et al., 2007) thereby contributing to the physical and chemical properties of the Eurasian Basin halocline and deeper waters (Jones and Anderson, 1986).

In the earliest study of the inorganic carbon cycle in the Arctic Ocean, Kelley (1970) directly observed undersaturated seawater pCO_2 across the Barents Sea with ΔpCO_2

values ranging from ~ -50 to $-150\,\mu$atm. More recently, other studies have shown seawater pCO_2 values of ~220–350 μatm with a seasonal minima occurring during the summertime (May to October) (Omar et al., 2003, 2007; Nakaoka et al., 2007). Given that the ΔpCO_2 values ranged from ~ -20 to $-110\,\mu$atm, the Barents Sea has a strong potential for significant uptake of CO_2 from the atmosphere.

Nakaoka et al. (2007) and Omar et al. (2007) estimated an annual ocean CO_2 uptake of $46\pm18\,\mathrm{g\,C\,m^{-2}\,yr^{-1}}$ and $51\pm8\,\mathrm{g\,C\,m^{-2}\,yr^{-1}}$, respectively, in the Barents Sea (Table 1), accounting for sea-ice cover during the wintertime. Using mass balance approaches, and accounting for the influence of phytoplankton primary production, freshwater inputs and mixing on vertical profiles of DIC and inorganic nutrients, Fransson et al. (2001) computed an annual ocean CO_2 uptake of $44\pm10\,\mathrm{g\,C\,m^{-2}\,yr^{-1}}$. Kaltin et al. (2002), using similar mass balance approaches applied to inorganic carbon data collected from a section across the Barents Sea estimated an ocean CO_2 uptake of $29+11\,\mathrm{g\,C\,m^{-2}}$ for 3 months of the year (i.e., May to July). For comparison, Takahashi et al. (2009) estimated a climatological mean uptake of $\sim$5–30 $\mathrm{g\,C\,m^{-2}\,yr^{-1}}$ from a very limited dataset of surface underway pCO_2 data, with the oceanic CO_2 sink decreasing in a general trend across the Barents Sea from the Atlantic Ocean inflow to the Kara Sea. Similar spatial trends were also observed by Kelley (1970), with ΔpCO_2 values generally increasing from $\sim -50\,\mu$atm close to the coastline to approximately $-150\,\mu$atm at the outer extents of the Barents Sea shelf.

The seasonal changes in surface pCO_2 and air-sea CO_2 exchange rates for the Barents Sea have been largely attributed to seasonal changes in phytoplankton primary production, warming and cooling, and air-sea CO_2 fluxes. In a general sense, cooling of surface waters during transit from the Atlantic Ocean to the Barents Sea throughout the year acts to decrease seawater pCO_2 at a thermodynamic rate of ~4.1% per °C (Takahashi et al., 1993; Millero et al., 1995). However, during the sea-ice free summertime, surface seawater pCO_2 decreases by ~100 μatm despite significant seasonal warming of the surface layer (~5–10°C) and ocean uptake of CO_2 through enhanced rates of air-sea CO_2 exchange. As Omar et al. (2007) suggest, these processes are more than

compensated for by summertime photosynthetic uptake of CO_2 by phytoplankton PP in the euphotic zone that acts to decrease seawater DIC and pCO_2. Indeed, the annual rate of net PP for the Barents Sea ranges from $\sim$ <9–100 g C m^{-2} yr^{-1} (Sakshaug, 2004; Macdonald et al., 2009), with rates of phytoplankton PP greater than other Arctic shelves with the exception of the Chukchi Sea.

The seasonal fall and winter rebound of seawater pCO_2 to values just below equilibrium with the atmosphere observed by Nakaoka et al. (2007) likely results from a continued uptake of CO_2 through gas exchange during sea-ice formation and brine rejection (Anderson et al., 2004; Omar et al., 2005) and vertical entrainment by mixing with CO_2 rich subsurface waters. Despite the absence of supporting data, it is likely that subsurface pCO_2 increases seasonally from fall and winter from the seasonal remineralization of organic matter, produced during earlier summertime enhanced rates of phytoplankton primary production, as observed in other Arctic Ocean marine environments (e.g., Yager et al., 1995; Bates et al., 2009).

4.1.2 Chukchi Sea shelf

The wide and shallow Chukchi Sea shelf, with the shelf break extending hundreds of kilometers northward from the coast, represents a particularly extensive portion of the Arctic shelf system. The Bering Strait acts as the gateway for Pacific Ocean waters to enter the Arctic Ocean via the Chukchi Sea (Coachman et al., 1975; Bjork, 1989). The mean annual inflow of Pacific water at Bering Strait is $\sim$0.8 Sv, with higher transport during the open-water sea-ice free season (Roach et al., 1975; Woodgate et al., 2005a, b; Woodgate and Aagaard, 2005), with minor inputs to the Chukchi Sea from the East Siberian Sea shelf via the intermittent Siberian Coastal Current through Long Strait (Weingartner et al., 1999). In general, there is a northward transport of water across the shallow Chukchi Sea shelf, with four major outflows ($\sim$0.1–0.3 Sv each; Woodgate et al., 2005a) from the Chukchi Sea into the Canada Basin and Beaufort Sea shelf through Long Strait, Central Channel, Herald Valley and Barrow Canyon (Paquette and Bourke, 1974; Weingartner et al., 1998, 2005; Woodgate et al., 2005b). As

with other Arctic Ocean shelves, physical transformations and seasonal sea-ice cover play a major role in shaping the Chukchi Sea shelf water-masses and ecosystem. During the sea-ice covered season, watermasses on the Chukchi Sea shelf are confined to a small range of temperature-salinity space due to vertical homogenization by ventilation, brine rejection and convective mixing (Woodgate et al., 2005a). During the sea-ice free season, local sea-ice melt contributes to Pacific Ocean water to produce relatively warm, fresher surface mixed layer water (upper 0–$\sim$30 m, salinity typically <31; temperature >−1.5) with denser resident winter water remaining in the subsurface. Inflow of inorganic nutrient rich Pacific water supports high rates of phytoplankton PP or NCP on the Chukchi Sea shelf compared to other Arctic shelves (>300 g C m^2 y^{-1} or 0.3–2.8 g C m^2 d^{-1}; Hameedi, 1978; Cota et al., 1996; Sambrotto et al., 1993; Hansell et al., 1993; Wheeler et al., 1996; Gosselin et al., 1997; Hill and Cota, 2005; Bates et al., 2005a; Mathis et al., 2009; Macdonald et al., 2009).

In early studies of the Chukchi Sea, Semiletov et al. (1999) observed undersaturated seawater pCO_2 ($\sim$200–350 μatm) during the sea-ice free period across the shelf with lowest values ($\sim$150–200 μatm) observed close to the ice edge at the northern shelf break. More recently, other studies have observed similar undersaturated seawater pCO_2 conditions from May to September ($\sim$150–350 μatm; Pipko et al., 2002; Murata and Takizawa, 2003; Bates et al., 2005a; 2006; Bates, 2006; Chen and Gao, 2007). Extremely low pCO_2 conditions (<100 μatm) were observed in the surface layer in the vicinity of Barrow Canyon at the northern edge of the Chukchi Sea shelf in a location with very high rates of phytoplankton primary production (Bates et al., 2005a; Hill and Cota, 2005). Early season observations under near complete sea-ice cover also indicate that Chukchi Sea shelf "winter" surface waters were not as undersaturated with respect to the atmosphere (ΔpCO_2 values of $\sim$−20–60 μatm) compared to the summertime sea-ice free period (Bates, 2006). In contrast to surface waters, subsurface waters seawater pCO_2 values were highly oversaturated with respect to the atmosphere (Bates, 2006; Bates et al., 2009).

Estimates of the rates of air-sea CO_2 exchange during the sea-ice free period in

the summertime have ranged from ~20–90 mmoles CO_2 m^{-2} d^{-1} (Wang et al., 2003; Murata and Takizawa, 2003; Bates, 2006). These studies indicate that the ocean uptake of CO_2 from the atmosphere is greater for the Chukchi Sea shelf than other Arctic shelves. However, in regions of the Chukchi Sea shelf where sea-ice cover remained high (>80%) during the summertime, air-sea CO_2 exchange rates were estimated to be generally low (<1 mmoles CO_2 m^{-2} d^{-1}; Bates, 2006). Similarly, wintertime air-sea CO_2 exchange rates during complete sea-ice cover were estimated to be minor (<1 mmoles CO_2 m^{-2} d^{-1}; Bates, 2006). The annual ocean CO_2 uptake for the Chukchi Sea shelf has been estimated at 24–108 g C m^{-2} yr^{-1} (Table 1; Bates, 2006). Similarly, using mass balance approaches, Kaltin and Anderson (2005) estimated that the annual ocean CO_2 uptake for the Chukchi Sea to be 86 ±22 g C m^{-2} yr^{-1}.

The seasonal changes in surface pCO_2 and strong sink for atmospheric CO_2 on the Chukchi Sea shelf have been largely attributed to cooling of surface waters during the northward transit of waters across the Chukchi Sea shelf (Murata and Takizawa, 2003) and high rates of summertime phytoplankton PP that acts to decrease seawater DIC and pCO_2 (Bates, 2006). As in the Barents Sea, the fall and winter rebound of seawater pCO_2 to values just below equilibrium with the atmosphere likely results from a continued uptake of CO_2 through gas exchange during sea-ice formation and brine rejection (Anderson et al., 2004; Omar et al., 2005) and vertical entrainment by mixing with CO_2 rich subsurface waters.

4.2 Arctic Ocean shelves: interior shelves

4.2.1 Siberian Sea shelves (i.e., Kara, Laptev and East Siberian Seas)

The Kara Sea shelf is controlled by exchanges with the Barents Sea and adjoining Eurasian Basin. Freshwater runoff from the Ob and Yenisey Rivers mix with more saline water of Atlantic origin, before entering the Laptev Sea or exported into the central basin of the Arctic Ocean (e.g., Anderson et al., 1994; Jones et al., 1998; Fransson

et al., 2001). The Laptev and East Siberian Sea shelves are subsequently controlled by exchanges with the adjoining Kara and Chukchi Seas, and major freshwater inputs to the Laptev Sea through the Lena River (e.g., Gordeev et al., 1996; Olsson and Anderson, 1997). On all of these shelves, seasonal sea-ice melt and formation, and brine rejection in coastal polynyas are important processes (e.g., Dmitrenko et al., 2008) with sea-ice production in this region occurring at the highest rate compared to other Arctic shelves. There is a general flow from the Laptev Sea across the East Siberian Sea and into the Chukchi Sea through the East Siberian Sea current (e.g., Weingartner, 1999; Nitishinsky et al., 2008), but circulation patterns can reverse with considerable transport from the East Siberian Sea shelf across the northeastern Laptev Sea shelf (e.g., Dmitrenko et al., 2008).

There have been few studies of inorganic carbon on the Siberian Sea shelves, with surface seawater pCO_2 and ΔpCO_2 values highly variable over time and space. During the sea-ice free period, surface waters of the Kara Sea appear to be undersaturated with respect to the atmosphere. Semiletov et al. (1999) report a range of 273–405 μatm for surface seawater pCO_2 while Kelley (1970) reported ΔpCO_2 values ranging from −30 to −100 μatm across much of the Kara Sea in 1967. In contrast, supersaturated surface seawater pCO_2 were observed nearshore and close to the outflow of the Ob and Yenisey Rivers (Kelley, 1970; Makkaveev, 1994; Semiletov et al., 1999). In the other Siberian Sea shelves, generally undersaturated surface seawater pCO_2 (216−~400 μatm) for the Laptev Sea and highly variable seawater pCO_2 conditions in the East Siberian Sea (~300–844 μatm) have been reported (Semiletov et al., 1999, 2007). On both shelves, supersaturated surface seawater pCO_2 values were observed for the Lena River that drains into the Laptev Sea and Kolyma Rivers that outflows to the East Siberian Sea shelf (Semiletov et al., 1999, 2007).

Fransson et al. (2001), using carbon mass balance approaches, computed a small annual ocean CO_2 uptake of 1 g C m^{-2} yr^{-1} for the Kara Sea (Table 1). For the Laptev Sea, mass balance assessments integrated across the shelf indicate that this sea is a sink for atmospheric CO_2 during the sea-ice free summertime (~2.1 mmoles C m^{-2} d^{-1};

July–September; Nitishinsky et al., 2008) despite supersaturated seawater pCO$_2$ conditions (i.e., sources of CO$_2$ to the atmosphere) in nearshore bays (Olsson and Anderson, 1997) and Lena River outflow (Semiletov et al., 1999, 2007). Direct eddy correlation measurements of air-sea CO$_2$ exchange in late summer (September) close to the multiyear sea-ice at the shelf break of the Laptev Sea yielded more contradictory results with air-sea CO$_2$ exchange rates varying from invasion (i.e., sink of CO$_2$; ~1.7 mmoles C m^{-2} d^{-1}) to evasion (i.e., source of CO$_2$; ~1.2 mmoles C m^{-2} d^{-1}; Semiletov et al., 2007). If we extrapolate the results of Nitishinsky et al. (2008) and assume a 100 d sea-ice free period, and negligible air-sea gas exchange during wintertime sea-ice cover, an annual ocean CO$_2$ uptake of ~2.4 g C m^{-2} yr^{-1} is computed (Table 1). For the East Siberian Sea shelf, the sink or source terms are uncertain. Nitishinsky et al. (2008) estimated that the East Siberian Sea shelf is a small source of CO$_2$ to the atmosphere (~0.3 mmoles C d^{-1}). However, Semiletov et al. (2007) suggest that the western area of the shelf is a source of CO$_2$ to the atmosphere (1±1.6 mmoles C d^{-1}, 2003; and 10.9±12.6 mmoles C d^{-1}, 2004) while the eastern area, influenced by mixing with Pacific Ocean water from the Chukchi Sea shelf, is a sink for atmospheric CO$_2$.

The above studies suggest that the Siberian Sea shelves range from minor sinks to minor sources of CO$_2$ to the atmosphere, with the causes uncertain at present. Nitishinsky et al. (2008) suggest that the drawdown of pCO$_2$ from summertime photosynthetic uptake more than compensates for seasonal warming, and mixing with river freshwater and high-CO$_2$ subsurface waters, all of which act to increase seawater pCO$_2$. Semiletov et al. (2007) showed highly supersaturated values for subsurface waters on all of the Siberian Sea shelves, presumably resulting from remineralization of organic matter introduced from the Siberian Rivers (e.g., Anderson et al., 1990; Cauwet and Sidorov, 1996; Kattner et al., 1999) and from vertical export of organic carbon despite relatively low rates of summertime phytoplankton primary production (compared to other Arctic shelves) in the euphotic zone (~6–12 g C m^{-2} yr^{-1}; Macdonald et al., 2009). The East Siberian Sea shelf may be more highly influenced by these processes

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and hence more likely to be net heterotrophic and a source of CO$_2$ to the atmosphere. The Laptev Sea also has a permanent flaw lead polynya (Nitishinsky et al., 2008) that may contribute to ocean CO$_2$ uptake from the atmosphere during wintertime brine rejection and sea-ice formation as shown elsewhere (Anderson et al., 2004; Omar et al., 2005).

4.2.2 Beaufort Sea shelf

The Beaufort Sea shelf has a relatively narrow (~50 km) continental shelf in contrast to the adjacent Chukchi Sea shelf. The eastern Beaufort Sea shelf is heavily influenced by outflow from the Mackenzie River, and this input of freshwater and terrigenous input dominates the physical and chemical properties of the Beaufort Sea shelf (Carmack and Macdonald, 2002; Macdonald et al., 2009). Compared to the adjacent Chukchi Sea shelf, annual rates of phytoplankton PP for the Beaufort Sea shelf were relatively low (~7–17 g C m^{-2} yr^{-1}; Macdonald et al., 2009), similar to other "interior" type shelves (Carmack and Wassman, 2006) such as the Siberian Sea shelves. In the adjoining Canada Basin, wind-driven, clockwise rotation of the Beaufort Gyre controls regional scale sea-ice and upper ocean circulation (Carmack and Chapman, 2003). Along the northern edge of the Chukchi and Beaufort Seas, a narrow eastward boundary current is present (Nikolopoulos et al., 2009) which is constrained to follow the isobaths along the shelf break due to strong dynamic controls (Winsor and Chapman, 2004; Spall, 2007). The generalized regional water circulation along the Beaufort Sea shelf is directed eastward with shelf waters principally renewed principally by Pacific Ocean waters that enter through Bering Strait and exit the Chukchi Sea off the Alaskan coast. Shelf-basin exchange facilitated by the generation of mesoscale eddies (Manley and Hunkins, 1985; Muench et al., 2000; Pickart et al., 2005; Mathis et al., 2007), and winter brine rejection during sea-ice formation are also important for these shelves.

As with the Siberian Sea shelves, few studies have been conducted on the Beaufort Sea shelf. Seawater pCO$_2$ conditions appear to be highly variable (~150–350 μatm) in the western part of the Beaufort Sea shelf (Murata and Takizawa, 2003; Bates, 2006).

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Extremely low seawater pCO_2 conditions ($<100\,\mu$atm) have also been observed in the surface layer of the Beaufort Sea shelf east of Point Barrow in a region of characterized by high proportions of freshwater (10–20%) and sea-ice melt (10–25%) (Cooper et al., 2005; Bates, 2006). Murata and Takizawa (2003) have estimated that rates of air-sea CO$_2$ exchange were relatively low ($-12\,$mmoles $CO_2\,$m$^{-2}\,$d^{-1}) during the summertime compared to the adjacent Chukchi Sea. In areas of the western Beaufort Sea shelf where sea-ice cover remained high (>80%), air-to-sea CO_2 fluxes were generally low ($<1\,$moles $CO_2\,$m$^{-2}\,$d^{-1}; Bates, 2006). The annual ocean CO_2 uptake for the Beaufort Sea shelf has been estimated at $1.2\,$g C m$^{-2}\,$yr^{-1}, low compared to other Arctic shelves (Table 1; Murata and Takizawa, 2003).

4.3 Arctic Ocean shelves: outflow shelves

4.3.1 Canadian Archipelago shelf

The shelf of the Canadian Archipelago has been poorly sampled for marine inorganic carbon cycle properties. There is little information to estimate rates of air-sea CO_2 gas exchange and the processes that control the inorganic carbon cycle. In the adjacent Hudson Bay, Else et al. (2008) observed mean rates of air-sea CO_2 exchange of $-0.7\,$mmoles $CO_2\,$m$^{-2}\,$d^{-1} during the sea-ice free period. On annual timescale, a small ocean CO_2 uptake for the Hudson Bay shelf is estimated at $0.07\,$g C m$^{-2}\,$yr^{-1} (Else et al., 2008).

In the CARINA dataset (Fig. 2), computation of pCO_2 from DIC and alkalinity datasets indicate that surface pCO_2 values ranged from $\sim$300–400$\,\mu$atm on the Canadian Archipelago shelf and generally undersaturated with respect to the atmosphere. During the CASES project in the early 2000's, surface pCO_2 values ranged from $\sim$300–430$\,\mu$atm with significant sptial variability (Mucci et al., 2008). If we assume that air-sea CO_2 exchange rates are similar for the Canadian Archipelago as the "upstream" Beaufort Sea shelf, the annual uptake for the Canadian Archipelago shelf is computed at

-16 to $-24\,$g C m$^{-2}\,$yr^{-1} (Table 1).

4.4 Arctic central basin: Canada and Eurasian basins

4.4.1 Canadian Archipelago shelf

The central basin of the Artic Ocean is strongly stratified (Kinney et al., 1970; Aagaard et al., 1985; Jones and Anderson, 1986; Anderson et al., 1989; Aagaard and Carmack, 1994; Anderson et al., 1994a, b; Schlosser et al., 1995; Codispoti et al., 2005). In the Eurasian and Canada Basin, surface waters of the central basin are derived from a mixture of local sea-ice melt, fresh water inputs, exchanges with shelf waters of Pacific Ocean and Atlantic Ocean origin (Jones et al., 2008). In the Canada Basin, a strong vertical density gradient separates nutrient poor surface waters or polar mixed layer (PML) from underlying nutrient rich halocline waters that can be subdivided into Upper Halocline Layer (UHL) and Lower Halocline Layer (LHL). The shelf surface waters and underlying upper halocline waters have a predominantly Pacific Ocean origin based on characteristic temperature, salinity (Aagaard et al., 1981), inorganic nutrient, dissolved oxygen, barium and alkalinity distributions (e.g., Wallace et al., 1987; Wilson and Wallace, 1990; Jones et al., 1991; Salmon and McRoy, 1994; Falkner et al., 1994; Anderson, 1995; Rudels et al., 1996; Guay and Falkner, 1997; Anderson et al., 1999; Jones et al., 2003). In surface waters of the Canada Basin, the river fraction can be up to 20% (Macdonald et al., 2002; Cooper et al., 2005), while localized to the upper few metres, the sea-ice melt fraction can also exceed 25% (Cooper et al., 2005) during the summertime retreat of sea-ice. In the Eurasian Basin, surface waters and halocline waters are predominantly of Atlantic Ocean origin that have been modified on the Barents Sea and Siberian Seas shelves adjacent to the Eurasian Basin (Anderson et al., 1994). The upper halocline layer is absent from most of the Eurasian Basin (Anderson et al., 1994). At greater depths of the central basin is the Atlantic Water Layer (AWL; $\sim$200–800 m deep) and the Arctic Ocean Deep Water (AODW), both of which have Atlantic Ocean origins (e.g., Jones et al., 1991, 1995).

The central basin of the Arctic has been poorly sampled for marine inorganic carbon cycle properties. The Arctic Ocean Section (AOS) expedition in 1994 sampled across the Eurasian Basin and Canada Basin, west of the Chukchi Cap (Anderson et al., 1998a). Calculation of pCO_2 from AOS DIC and TA data (obtained at http://cdiac.ornl.gov/) indicate that the surface waters had seawater pCO_2 values of $\sim$300–330 μatm and ΔpCO_2 values of $\sim -40 - 70\,\mu$atm, and hence undersaturated with respect to the atmosphere. In the Canada Basin, adjacent to the Chukchi Sea shelf, lower seawater pCO_2 values of $\sim 240 - 280\,\mu$atm and ΔpCO_2 values of $\sim -150\pm25\,\mu$atm have also been observed (Bates, 2006; Bates et al., 2006). These observations suggest that the central basin of the Arctic Ocean has the potential to absorb significant amounts of CO_2 (Kaltin and Anderson, 2001; Bates et al., 2006). The capacity for sea-ice to allow direct gas exchange is debated (e.g., Gosink et al., 1976; Semiletov et al., 2004; Delille et al., 2007; Nagurnyi, 2008) and we assume that sea-ice is an effective barrier to gas exchange. In regions of the Canada Basin with 100% sea-ice cover, Bates et al. (2006) estimated an air-sea CO_2 exchange of $<3\,\mathrm{mmoles\,CO_2\,m^{-2}\,d^{-1}}$ through leads, fractures and brine channels, with much higher rates of exchange in areas without complete sea-ice cover.

4.5 Arctic Ocean (shelves and central basin): annual air-sea CO_2 exchange rate estimates

Early carbon mass balance estimates of the rate of air-sea CO_2 exchange suggested that the entire Arctic Ocean was a sink for CO_2 in the range of -70 to $-129\,\mathrm{Tg\,C\,year^{-1}}$ (Table 1: Anderson et al., 1990, 1994; Lundberg and Haugen, 1996). Subsequently, Anderson et al. (1998b) and Kaltin and Anderson (2005) used similar carbon mass balance approaches but revised their estimates of the Arctic Ocean CO_2 sink downward to -24 and $-31\,\mathrm{Tg\,C\,year^{-1}}$. More recently, direct ΔpCO_2 observations and air-sea CO_2 exchange rate estimates revised the Chukchi Sea shelf CO_2 sink upward and the Arctic Ocean CO_2 sink was estimated at $66\,\mathrm{Tg\,C\,year^{-1}}$ (Bates, 2006; Bates et al., 2006). A

review of published data suggests that the Arctic Ocean CO_2 sink ranges from approximately -65 to $-175\,\mathrm{Tg\,C\,year^{-1}}$ depending on lowest to highest flux rates estimates from available studies (Table 1). In the absence of data, if the area of the Canadian Archipelago is scaled to air-sea CO_2 exchange rates observed in the adjacent and "upstream" Beaufort Sea shelf, estimates of the Arctic Ocean CO_2 sink increase and range from approximately -81 to $-199\,\mathrm{Tg\,C\,year^{-1}}$ (Table 1). In comparison to the mean annual global ocean CO_2 uptake of approximately $-1400\,\mathrm{Tg\,C\,year^{-1}}$ (Takahashi et al., 2009), the Arctic Ocean CO_2 sink potentially contributes $\sim 5-14$% to the global balance of CO_2 sinks and sources.

5 Feedbacks and vulnerabilities

The Arctic Ocean is currently in the forefront of climate change caused by both natural and anthropogenic factors that influence the cryosphere, hydrological and biogeochemical cycles of the Arctic. However, due to undersampling of the Arctic Ocean, many uncertainties remain about the marine carbon cycle and, as shown earlier in this review, the uptake of CO_2 and the physical and biological processes that control the inorganic carbon cycle on the shelves and in the central basin. It is thus difficult to quantitatively predict changes in processes and feedbacks in the Arctic Ocean. However, here we discuss the potential vulnerabilities of the inorganic carbon cycle due to natural and anthropogenic factors, including: (1) sea-ice loss; (2) warming, circulation and other physical changes; (3) changes in biology and ecosystem structure of the surface and halocline water, and; (4) changes in the hydrological cycle and freshwater inputs to the Arctic Ocean.

5.1 Sea-ice loss

Mean air temperatures over the Arctic have increased by $\sim 2 - 3\,^{\circ}$C in summertime and by $\sim 4\,^{\circ}$C in winter since the 1950's (Chapman and Walsh, 2003) with projections for

a further 4–5°C increase by the end of the 21st century (ACIA, 2005). In conjunction with these higher temperatures, sea ice cover in the Arctic Ocean has contracted over the past three decades (Levi, 2000; Parkinson, 2000; Cavalieri et al., 2003; Wang et al., 2005; Overland and Wang et al., 2005; Rothrock and Zhang, 2005; Stroeve et al., 2005, 2007), with the pace of decline accelerating beyond model predictions over the last several years (Winton, 2006; Holland et al., 2006; Overland and Wang, 2007; Stroeve et al., 2007; Maslanik et al., 2007). The length of the seasonal sea-ice melt period has declined (e.g., Smith 1998; Rigor et al., 2002; Rigor and Wallace, 2004; Arrigo et al., 2008; Comiso et al., 2008) and sea-ice thickness observed over the central Arctic Ocean has decreased as thick multi-year sea-ice is replaced by thinner first-year sea-ice (e.g., Rothrock et al., 1999; Giles et al., 2008). The decline in Arctic sea-ice cover has been attributed to a combination of factors, including: (1) increased Arctic temperatures (Rothrock and Zhang, 2005: Lindsay and Zhang, 2005); (2) increased advection of warmer water into the Arctic Ocean from the Atlantic Ocean through the Fram Strait and Barents Sea gateways (Steele and Boyd, 1998; Dickson et al., 2000) and from the Pacific Ocean through Bering Strait (Maslowski et al., 2001; Shimada et al., 2006, 2007), and; (3) increased advection of sea-ice out of the Arctic Ocean through Fram Strait due to recent changes in atmospheric circulation patterns (Rigor and Wallace, 2004; Maslanik et al., 2007: Serreze et al., 2007). In combination, these factors contribute to a positive feedback where sea-ice loss reinforces surface warming due to reduced surface albedo and increased shortwave penetration, which in turn inhibits sea-ice formation in wintertime and allows for acceleration of sea-ice loss during the summertime (Perovich et al., 2007).

The loss of sea-ice is expected to both reduce the % sea-ice cover and expose undersaturated surface waters of the Arctic shelves and central basin (i.e., Canada and Eurasian Basins). Prior to 2007, the rate of sea-ice loss from the central Arctic Ocean was estimated at $\sim$36 000 km^2 $year^{-1}$ (Cavalieri et al., 2003). In surface waters of the Canada Basin, a mean ocean CO_2 uptake of 46±8 mmoles CO_2 m^2 d^{-1} was observed in 2002 and 2004 in sea-ice free areas during summertime. These air-sea

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CO_2 exchange rates were scaled to the entire central basin and annual reduction of sea-ice extent to estimate an increase of the ocean CO_2 sink of 2.0±0.3 Tg C $year^{-1}$ due to sea-ice loss with the effect compounding over time (Bates et al., 2006). In 2007 and 2008, sea-ice extent reached a seasonal minima 25% lower than any previously observed in the satellite record (Maslanik et al., 2007; Comiso et al., 2008) constituting an additional exposure of $\sim$600 000 km^2 of surface waters to air-sea gas exchange. Assuming a *status quo* of inorganic carbon distributions in surface waters of the Arctic, this recent loss of summertime sea-ice may have increased the ocean uptake of CO_2 in the Arctic by an additional 33±10 Tg C $year^{-1}$. If sea-ice cover was lost completely over the central basin during summertime, surface waters of the Arctic Ocean might absorb an additional $\sim$280 to 1200 Tg of CO_2 (Anderson and Kaltin, 2001; Bates et al., 2006). The range of estimates depends on differences in surface water carbonate chemistry observed between the Canada Basin and Eurasian Basin. For example, Anderson and Kaltin (2001) computed how much CO_2 was needed to equilibrate the surface mixed layer with the atmosphere using vertical profiles of DIC data from the Eurasian Basin.

The above estimates of CO_2 uptake changes due to sea-ice loss have many uncertainties and associated caveats. These studies are only applicable to the near-term future (<decade) since it was assumed that the driving force of gas exchange (e.g., ΔpCO_2 and DIC distributions of surface and underlying halocline layer waters) would not change significantly over the residence time of surface waters in the Arctic (e.g., 2–30 years; Macdonald et al., 2009). However, in the era of rapid change in the Arctic, inorganic carbon distributions and air-sea CO_2 exchange rates are highly likely to change due to a host of other factors. Since the effect of these other factors on the marine inorganic carbon cycle can be opposing or amplifying in nature, future predictions of the trajectory of the Arctic Ocean CO_2 sink/source terms are difficult to make.

5.2 Warming, circulation and other physical changes in the Arctic

Due to simple thermodynamics, warming should increase seawater pCO_2 at a rate of ~4.1% per °C (Takahashi et al., 1993; Millero et al., 1995). In the central basin, if we assume present day surface water pCO_2 values of 250–300 μatm, a 1°C warming should increase seawater pCO_2 by ~8–12 μatm per 1°C and reduce ΔpCO_2 values and the ocean CO_2 sink by ~10%. In the recent past (1998–2006), Pabi et al. (2008) observed positive anomalies in surface temperatures of up to 2°C in the regions of significant sea-ice loss (mainly on the "inflow" Arctic shelves). If surface waters equilibrate with the predicted 4–5°C warming of the atmosphere over the Arctic by the end of the 21st century (ACIA, 2005), and if present-day inorganic carbon distributions remain unchanged, the Arctic Ocean CO_2 sink might reduce by ~40–50% due to warming.

The loss of sea-ice in the Arctic should result in greater open water area, and increased air-sea interaction, with a variety of consequences. At the same time, increased latitudinal atmospheric gradients could result in increased windspeed and storm events over the Arctic. Although the direction of air-sea gas exchange is forced by ΔpCO_2 values, the rate of gas exchange of CO_2 and other gases is primarily driven by windspeed and atmospheric boundary layer-surface water interactions. Given these dictates, even though ΔpCO_2 values might reduce, air-sea CO_2 gas exchange rates can increase since gas transfer velocities increase exponentially relative to windspeed (Wanninkhof, 1992; Wanninkhof and McGillis, 1999) and CO_2 flux in other regions can be dominated by storms and high-wind events (Bates and Merlivat, 2001).

Wind-driven air-sea interaction and eddy formation may also change, including wind-induced upwelling/downwelling (Melling, 1993; Pickart et al., 2006, 2009) and formation of eddies that contribute to exchanges of water and materials between the shelf and basin (Manley and Hunkins, 1985; Muench et al., 2000; Pickart et al., 2005), particularly in the western Arctic between the Beaufort Sea shelf and Canada Basin (Carmack and Macdonald, 2002; Mathis et al., 2007; Spall et al., 2008). Wintertime sea-ice is thinner and there may be potentially greater air-sea gas exchange through

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sea-ice (Gosink et al., 1978; Semiletov et al., 2004; Delille et al., 2007) with sea-ice a potentially weaker barrier to gas exchange. In wintertime, wind-driven polynyas open up on the Chukchi and Laptev Sea shelves in particular (Cavalieri and Martin, 1994; Nitishinsky et al., 2007), resulting in the formation of dense water via brine-driven convection (Weingartner et al., 1998). Since brine rejection and formation of dense water appears to facilitate uptake of CO_2 from the atmosphere (Anderson et al., 2004; Omar et al., 2005), enhanced opening of polynyas and leads may increase the sink of CO_2 in the Arctic in the near-future depending on inorganic carbon distributions and future air-sea CO_2 disequilibrium. However, the cumulative effect of the present influence and future changes in these processes remain uncertain.

5.3 Changes in biology and ecosystem structure in surface and halocline waters of the Arctic Ocean

The loss of sea-ice in the Arctic and greater open water area should also enhance upwelling at the shelf-break and potentially increase the input of nutrients from subsurface waters to the Arctic shelves (ACIA, 2005). The growing season for phytoplankton should increase with reduced sea-ice extent and longer open-water conditions. As a consequence of increased phytoplankton PP or NCP, the drawdown of pCO_2 and DIC should increase the air-sea CO_2 disequilibrium (i.e., ΔpCO_2) and increase the net oceanic uptake of CO_2 (Anderson and Kaltin, 2001; Bates et al., 2006). Recent reductions of sea-ice cover, particularly in the western Arctic Ocean, have resulted in a longer phytoplankton growing season and a ~30–60% increase in primary production over the last decade, with a ~10–40% increase in phytoplankton primary production over the last several years (Arrigo et al., 2008). For sea-ice communities that generally account for a relatively small fraction of primary production, the reduction of sea-ice extent and thickness will reduce the contribution of sea-ice algae to primary production (Subba Rao and Platt, 1984; Legendre et al., 1992; Gosselin et al., 1997) and their influence on surface water inorganic carbon distributions and air-sea CO_2 disequilibrium.

Other factors may also influence the marine inorganic carbon cycle and present-day

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CO_2 sink in the Arctic Ocean. For example, reduced sea-ice cover has been proposed to favor a "phytoplankton-zooplankton" dominated ecosystem rather than a "sea-ice algae–benthos" dominated ecosystem over the Arctic shelves (Piepenburg, 2005). At present on the highly productive Chukchi Sea shelf, ~10% of NCP is converted to dissolved organic carbon (DOC) and ~15% of NCP is converted to suspended particulate organic carbon (POC) (Mathis et al., 2007b, 2009) that gets exported from the shelf into the Canada Basin beneath the mixed layer (Bates et al., 2005b). The remaining 75% of NCP is exported from the mixed layer to the sea floor as sinking particles that sustain the rich benthos on the sea floor of the Chukchi Sea shelf (Grebmeier et al., 2007). In the Bering Sea, earlier sea-ice loss has led to ecosystem changes and altered pelagic-benthic coupling (e.g., Stabeno et al., 2001, 2002; Hunt et al., 2002; Overland et al., 2001; Napp et al., 2002; Bond et al., 2003; Merico et al., 2004). If there are ecosystem shifts in the future, for example on the Chukchi and Beaufort Seas shelves, the export of organic carbon and pelagic-benthic coupling might decrease, despite concurrent increases in phytoplankton PP.

There may also be changes in the inorganic carbon distributions of subsurface waters on the Arctic shelves and halocline layer waters of the central basin. In the central basin, density stratification generally acts as a barrier to mixing between nutrient-poor surface waters and nutrient-rich deep waters (Aagaard et al., 1981; Jones and Anderson, 1986). Halocline waters generally have much higher pCO_2 and DIC content than surface waters (Jutterstrom and Anderson, 2004), with low rates of upward vertical diffusion between these waters and the surface mixed layer (Wallace et al., 1987; Wilson and Wallace, 1990; Bates, 2006). The mixed layer typically extends to 10–50 m, with depth heavily dependent on seasonality of winds and sea-ice cover (Carmack and Macdonald, 2002). The reduction of sea-ice extent may facilitate deeper mixing and erosion into inorganic nutrient and CO_2 rich halocline waters. Depending on the stoichiometry of nutrients and carbon entrained into the mixed layer, enhancement of phytoplankton PP in typically highly oligotrophic surface waters of the Arctic (e.g., English, 1961) and subsequent vertical export of organic carbon, this mechanism could

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either enhance or suppress air-sea CO_2 disequilibrium and CO_2 exchange between atmosphere and ocean. The halocline is believed to ventilate predominantly through lateral processes and the transfer of water from the shelves into the interior formation of dense water on the shelves via brine-driven convection (Weingartner et al., 1998).

If the marine inorganic carbon cycle on the Arctic shelves is altered, the transfer of inorganic and organic carbon into the halocline may also change. For example, if there is increased transport of DOC from the shelves into the subsurface halocline of the central basin, remineralization of DOC by the microbial community may enhance pCO_2 and DIC contents of surface waters, and in turn, the upward supply of CO_2 to the surface layer through vertical diffusion and mixing. The release of alkalinity from the sediments, produced by anaerobic microbial decomposition, may also be important for suppressing seawater pCO_2 contents that could in turn enhance air-sea CO_2 disequilibrium (Thomas et al., 2009). Thus ecosystem changes in the Arctic shelves and in the central basin, both in the surface and underlying halocline layer, may alter inorganic carbon distributions and the CO_2 sink or source terms of the Arctic as a whole.

5.4 Changes in the hydrological cycle and freshwater inputs to the Arctic Ocean

Significant changes in the hydrological cycle of the Arctic are also predicted by the end of the 21st century (ACIA, 2005). Freshwater inputs from Arctic rivers and the transport of sediment and dissolved materials are expected to increase. At present, Arctic rivers influence the hydrographic properties of the Siberian Sea and Beaufort Sea shelves in particular. The eastern Beaufort Sea shelf is heavily impacted by Mackenzie River inflow of freshwater (e.g., Macdonald et al., 1995a, b; 2002, 2009; Kadko and Swart, 2005) and plumes of elevated sediment loads and chromophoric dissolved organic matter (CDOM) can be followed from the Mackenzie outflow into the Canada Basin using satellite remote sensing. However, the impact of increased river flow on the chemical characteristics of the Arctic is uncertain at present. The freshwater input of DOC will presumably increase, but its contribution to inorganic carbon distributions on the shelves from bacterial remineralization of DOC to CO_2 is highly dependent on the

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lability of DOC and its decomposition relative to residence times in the Arctic. While most riverine DOC is thought to be highly refractory (Hansell et al., 2004), enhanced open-water may increase the photochemical breakdown of refractory DOC to CO_2 in surface waters.

5.5 Summary of near-term impacts on Arctic Ocean air-sea CO_2 fluxes

In the near-term, sea-ice loss is expected to increase the uptake of CO_2 by surface waters because the exposed surface waters have a lower CO_2 content than the atmosphere. The loss of sea-ice in the Arctic also is likely to result in greater open water area, and increased air-sea interaction, with the likelihood of increased rates of air-sea gas exchange. Wintertime sea-ice is now thinner than previous decades and there may be potentially greater atmosphere-ocean gas exchange directly through sea-ice, with sea-ice a potentially weaker barrier to gas exchange. As a consequence of increased phytoplankton growth due to sea-ice loss and expansion of open water in the Arctic, the potential for the Arctic Ocean to uptake CO_2 should also increase.

In mitigation, reduced cooling of water during transit poleward and increased absoption of solar radiation resulting in warming of surface water relative to previous decades should act to increase the CO_2 content of seawater. This process may somewhat counteract the impacts of sea-ice loss and increased phytoplankton growth on the atmosphere-ocean exchange of CO_2.

6 Ocean acidification effects and changes in carbonate mineral saturation states

As a consequence of the ocean uptake of anthropogenic CO_2, surface $p CO_2$ and DIC concentration have increased while pH has decreased in the upper ocean over the last few decades (e.g., Winn et al., 1994; Bates et al., 1996; Bates, 2007; Bates and Peters, 2007; Takahashi et al., 2009). This gradual process, termed *ocean acidification*,

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has long been recognized (e.g., Broecker and Takahashi, 1966; Broecker et al., 1971; Bacastow and Keeling, 1973). Estimates based on the Intergovernmental Panel on Climate Change (IPCC) projections of future CO_2 emission and subsequent ocean absorption of anthropogenic CO_2 (Solomons et al., 2007) predict that upper ocean pH will decrease by 0.3–0.5 units over the next century and beyond (Caldeira and Wickett, 2003, 2005; Doney, 2006). The effects of ocean acidification are potentially far-reaching in the global ocean, particularly for calcifying fauna (e.g., Buddemeier et al., 2004; Royal Society, 2005; Fabry et al., 2008) with model studies suggesting that $CaCO_3$ mineral undersaturation due to ocean acidification should impact the Arctic before other regions(Orr et al., 2005; Steinacher et al., 2009).

The predicted worldwide pH changes using the A2 scenario (IPCC, 2007) are expected to increase hydrogen ion concentration by 185% and decrease pH by 0.45 (Steinacher et al., 2009). Decreased pH reduces the saturation states (Ω) of calcium carbonate ($CaCO_3$) minerals such as aragonite and calcite, and increases the potential for reduced production of $CaCO_3$ by calcifying fauna (e.g., Buddemeier et al., 2004; Royal Society, 2005; Fabry et al., 2008; Doney et al., 2009) and dissolution of $CaCO_3$ in the water-column and sediments.

In the Arctic Ocean, sea-ice melt, river runoff and phytoplankton photosynthesis and respiration appear to be the dominant processes that induce divergent directions for $CaCO_3$ saturation states for surface and subsurface waters. As such, these processes may suppress or enhance Ω values that in turn amplify or mitigate the impacts of ocean acidification in the Arctic.

6.1 Suppression and enhancement of Ω in surface waters

In surface waters, freshwater contributions from sea-ice melt and river runoff appear to be the primary processes that act to decrease $CaCO_3$ saturation states. Salisbury et al. (2008) have shown that the Ω values of major Arctic rivers are close to zero for the run-off end-member. In the Chukchi Sea and Canada Basin, surface mixed layer waters were generally saturated with respect to aragonite ($\Omega_{aragonite}$) but $\Omega_{aragonite}$ values

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decreased as runoff fraction increased (Bates et al., 2009). These findings are consistent with observations that a wide variety of Arctic rivers are net heterotrophic (e.g., Chen and Borges, 2009) with high pCO_2 contents (Kelley, 1970; Makkayeev, 1994; Semiletov, 1999; Semiletov et al., 2007; Nitishinsky et al., 2007) and corresponding low Ω values. River DOC remineralization and respiration in combination with many Arctic rivers having high TA contents (Anderson et al., 1983; Olsson and Anderson, 1997; Cooper et al., 2008; Bates et al., 2009) act to decrease Ω values.

Ω values have also been observed to decrease with increasing sea-ice melt fraction (>15%; Bates et al., 2009), and in a few localized surface areas in the Canada Basin, both aragonite and calcite undersaturation have been observed. Similarly, Chierici and Fransson (2009) have observed localized areas where surface waters were undersaturated with respect to aragonite ($\Omega_{aragonite}$) on the Canadian Archipelago and Beaufort Sea shelves which they attribute to the influence of freshwater contributions from sea-ice melt and river runoff. Cooling and air-sea uptake of CO_2 (which increases pCO_2 and DIC) will also act to decrease Ω values, but are relatively minor impacts compared to sea-ice melt and river runoff inputs to the Arctic. Low Ω values have also been attributed to upwelling of CO_2-rich subsurface waters off the Chukchi Sea shelf (Chierici and Fransson, 2009).

Oversaturated Ω values are been observed for surface waters across much of the Chukchi Sea shelf and adjacent Canada Basin (Jutterstrom and Anderson, 2005; Bates et al., 2009; Chierici and Fransson, 2009). The oversaturated conditions for both aragonite and calcite have been attributed to the high rates of phytoplankton PP that decrease pCO_2 and DIC, and increase Ω values on the Chukchi Sea shelf (Bates et al., 2009), as well as low DIC:TA ratios and Revelle Factors present in the Canada Basin (Bates, 2006) that facilitates oversaturated Ω conditions.

6.2 Suppression of Ω in subsurface waters

In the North Pacific Ocean, Feely et al. (1988) observed seasonal enhancement of surface Ω values and suppression of subsurface Ω values due to seasonal phytoplankton

PP, export of organic matter and subsequent remineralization to CO_2. A similar mechanism occurs in the Chukchi Sea where high rates of summertime phytoplankton PP (Hill and Cota, 2005; Bates et al., 2005; Mathis et al., 2009), vertical export of organic carbon (Lepore et al., 2007) and buildup of CO_2 in subsurface waters (primarily through subsurface remineralization of OM to CO_2, and benthic respiration) suppresses Ω values below saturation. Subsurface waters were observed to be undersaturated with respect to aragonite and calcite, and thus potentially corrosive to $CaCO_3$ for the Chukchi Sea shelf sediments and benthic ecosystem.

6.3 Amplification and mitigation of ocean acidification impacts in the Arctic Ocean

In many oceanic basins, the oceanic uptake of anthropogenic CO_2 has resulted in the shoaling of the aragonite saturation horizon (i.e., $\Omega_{aragonite}=1$) by 40 to 200 m (Feely et al., 2004) over the past century. Given the scenarios for pH changes in the Arctic Ocean (Orr et al., 2005; Steinacher et al., 2009), the Arctic shelves will be increasingly impacted by ocean acidification and presence of $CaCO_3$ mineral undersaturated waters. Superimposed on the ocean acidification effects induced by ocean uptake of anthropogenic CO_2, seasonal biological processes are likely to mitigate (enhance Ω) and amplify (suppress Ω) the impacts of ocean acidificaiton on the Arctic shelves.

The seasonal changes in Ω induced by biology primarily have been described as a seasonal "Phytoplankton-Carbonate Saturation State" (PhyCASS) interaction that drives divergent trajectories for carbonate chemistry in surface and subsurface waters of Arctic shelves like the Chukchi Sea (Bates et al., 2009). For inflow shelves (Carmack and Wassmann, 2006) like the Chukchi Sea and Barents Sea, high rates of summertime phytoplankton PP or NCP and vertical export of OM during seasonal sea-ice loss may drive a strong seasonal divergence in surface and subsurface Ω. The seasonal divergence in Ω is probably attenuated in the Barents Sea compared to the Chukchi Sea due to the presence of a deeper shelf. For interior shelves such as the Siberian and Beaufort Sea shelves, much lower rates of summertime phytoplankton PP, and

much greater influence of river runoff (with lower Ω) is also likely to result in attenuated divergence in Ω for surface and subsurface waters compared to the Chukchi Sea. On all shelves, a combination of Pacific or Atlantic water inflow and wintertime homogenization of shelf waters through wind-mixing and brine rejection proceses are likely to "rectify" the seasonal divergences in Ω between surface and subsurface waters.

In an era of rapid change in the Arctic, sea-ice loss, surface warming and increased phytoplankton PP on the Arctic shelves may act to enhance surface Ω and suppress subsurface Ω amplifying the existing impact of ocean acidification. This may be mitigated somewhat by increased freshwater contributions through sea-ice melt and river runoff that suppress surface water Ω. In the central basin of the Arctic Ocean, potentially corrosive waters to aragonite and calcite are found in the upper halocline layer (Jutterstrom and Anderson, 2005; Bates et al., 2009), with highly saturated Ω values in surface water. Increased air-sea interaction in regions experiencing continued seasonal sea-ice loss will likely exhibit increased vertical mixing of CO_2-rich subsurface waters, increased shelf-basin exchanges and ocean uptake of CO_2 through gas exchange. Combined, these factors will reduce the vertical gradients of Ω between surface and subsurface with the net result of suppressing surface Ω over the residence time of surface water in the central basin (2–30 years; Macdonald et al., 2009).

7 Conclusions

At present, the Arctic Ocean continental shelves and central basin have lower CO_2 content than the atmosphere, and these areas are potential sinks of CO_2 from the atmosphere. There are however localized areas of sea-ice melt and river inputs where the opposite is observed, and these areas are potential sources of CO_2 to the atmosphere. The CO_2 chemistry of the Arctic Ocean is highly influenced by physical and biological processes such as seasonal phytoplankton PP during summertime sea-ice retreat towards the pole, as well as temperature effects (both cooling and warming), shelf-basin exchanges and formation of dense winter waters, and river inputs of freshwater and carbon.

Although seasonal sea-ice cover provides a barrier to atmosphere-ocean gas exchange, the Arctic Ocean is a sink for CO_2, on the order of -65 to $-175\,\mathrm{Tg\,C\,year^{-1}}$, contributing 5–14% to the global balance of CO_2 sinks and sources. The Arctic Ocean has become an important influence on the global carbon cycle, with the marine carbon cycle and atmosphere-ocean CO_2 exchanges sensitive to Arctic Ocean and global climate change feedbacks. In the near-term, further sea-ice loss and increases in phytoplankton PP rates are expected to increase the uptake of CO_2 by Arctic surface waters, although mitigated somewhat by warming in the Arctic. Thus, the capacity of the Arctic Ocean to uptake CO_2 is expected to increase and alter in response to environmental changes driven largely by climate. These changes are likely to continue to modify the physics, biogeochemistry, and ecology of the Arctic Ocean in ways that are not yet fully understood. Finally, in response to increased phytoplankton PP and uptake of human-produced CO_2, the benthic ecosystem of the Arctic shelves are expected to be negatively impacted by ocean acidification which reduces the ability of many species to produce calcium carbonate shells or tests with profound implications for Arctic marine ecosystems.

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Table 1. Areas, depths, residence times, air-sea CO_2 exchange rates expressed in mmoles $C\,m^{-2}\,d^{-1}$ and $g\,C\,m^{-2}\,d^{-1}$, and annual air-sea CO_2 exchange rate expressed in Tg C ($10^{12}\,g\,C$). Negative air-sea CO_2 exchange rates indicates ocean uptake of CO_2 (i.e., CO_2 sink).

|	Area[a] (km²)	Depth[a] (m)	Residence[a] (years)	Air-Sea CO_2 flux C m⁻² d⁻¹	Air-Sea CO_2 flux (mmoles (g C m⁻² yr⁻¹)	Annual[f] CO_2 flux (Tg C yr⁻¹))	Reference
Barents Sea	1 512 000	200	1[b]	n/a	−46±18	−70±27	Nakaoka et al. (2007)
				n/a	−51±8	−77±12	Omar et al.2007
				n/a	−44±10	−67±15	Fransson et al. (2001)[g]
				n/a	−29±11	−44±16	Kaltin et al. (2002)[g]
Kara Sea	926 000	131	2.5	n/a	−1	−1.0	Fransson et al. (2001)[g]
				n/a	n/a	−5.7	Anderson et al. (1998a, b)[g]
Laptev Sea	498 000	48	3.5±2	−2.1	−2.4	−1.2	Nitishinsky et al. (2007)[g]
				n/a	n/a	−4.3	Anderson et al. (1998a, b)[g]
East Siberian Sea	987 000	58	3.5±2	−1 to −10.9	n/a	−1.2/−13	Semiletov et al. (2007)
				+0.3	n/a	+0.3	Nitishinsky et al. (2007)[g]
				n/a	n/a	−5.9	Anderson et al. (1998a, b)[g]
Chukchi Sea	620 000	80	0.2–1.2	−12	−17[d]	−11	Murata and Takizawa (2003)
				−40±22	−48±10[d]	−36±6	Bates et al. (2006)
				n/a	−61±10[e]	−46±6	Bates et al. (2006)
				n/a	−86±22	−53±14	Kaltin and Anderson (2001)[g]
Beaufort Sea	178 000	124	0.5–1.0	n/a	n/a	−2.9	Anderson et al. (1998a, b)[g]
				−12	−17[d]	−2	Murata and Takizawa (2003)
Canadian Archipelago	1 490 000	290	0.5–12	?	?	−16/−24	scaled to Beaufort Sea shelf
Central basin	4 489 000	2748	2–30[c]	<−1 to −3	−4 to −12	−6 to −19	Bates et al. (2006)
Arctic Ocean	10 700 000					−65	low estimate from above
						−175	high estimate from above
						−81	low estimate from above[k]
						−199	high estimate from above[k]
Arctic Ocean (other studies)						−129±65	Anderson et al. (1990)[g]
						−70±65	Anderson et al. (1994)[g]
						−110	Lundberg and Haugen (1996)[g,h]
						−24±17	Anderson et al. (1998b)[g]
						−41±18	Anderson et al. (1998b)[g,i]
						−31	Kaltin and Anderson (2005)[g]
						−66	Bates (2006)

Notes: [a] Macdonald et al. (2009) estimates of shelf areas, mean depth (m) and residence times; [b] Kaltin et al. (2002) estimate of Barents Sea shelf water residence time; [c] residence time of surface and halocline waters (upper 0–300 m only) from Macdonald et al. (2009); [d] summertime open water only (~100 d); [e] including wintertime air-sea CO_2 exchange; [f] annual flux estimated from annual uptake (g C yr⁻¹) multiplied by area of Arctic shelf from Macdonald et al. (2009); [g] mass balance assessment; [h] includes Norwegian Sea (Lundberg and Haugen, 1996); [i] includes river contribution (Anderson et al., 1998b), and; [k] includes air-sea CO_2 exchange rates for the Canadian Archipelago scaled to estimates of the Beaufort Sea shelf.

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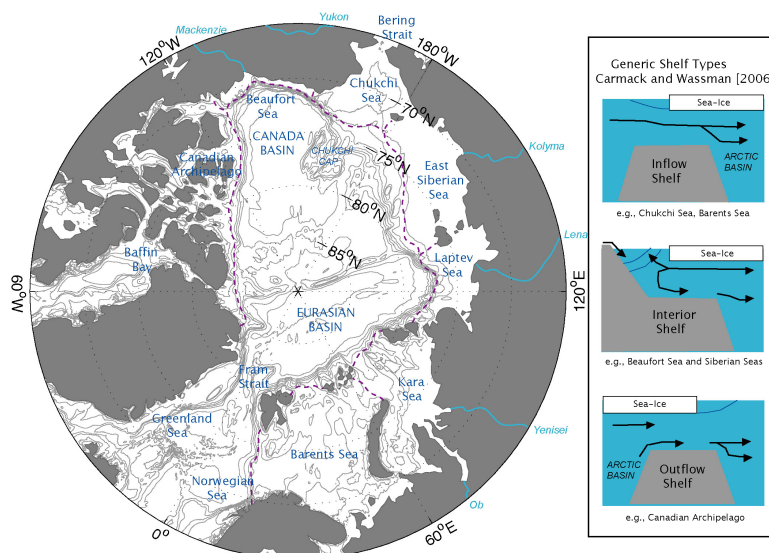
Fig. 1. Schematic of the Arctic Ocean, central basin (Canada and Eurasian Basins) and Arctic continental shelves (with approximate boundaries of each Arctic shelf sea), and major rivers draining into the region. Inset: characterization of Arctic Ocean continental shelves according to Carmack and Wassman (2006).
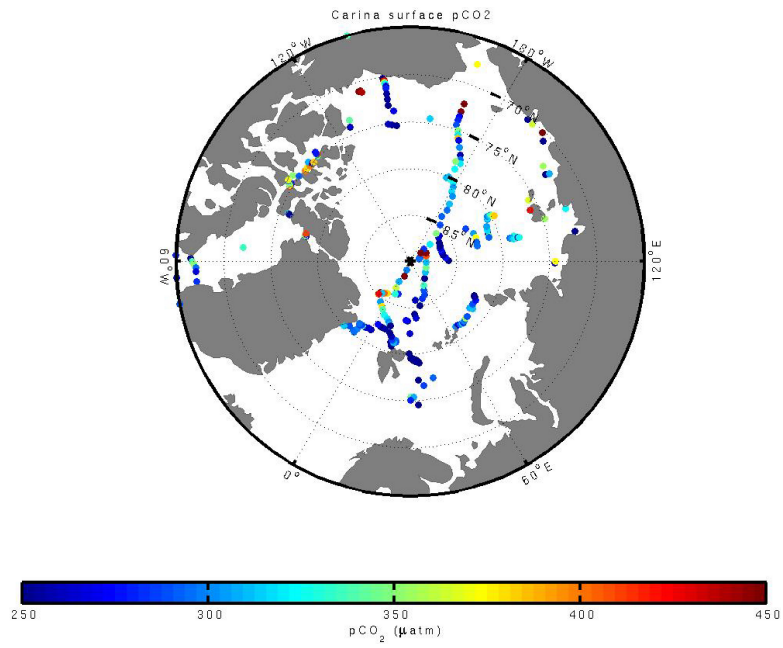
Fig. 2. Surface seawater pCO_2 values computed from DIC and TA data collected in the Arctic Ocean and part of the CARINA dataset (data obtained at http://cdiac.ornl.gov/).

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