



## An increasing CO<sub>2</sub> sink in the Arctic Ocean due to sea-ice loss

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[1] The Arctic Ocean and adjacent continental shelf seas such as the Chukchi and Beaufort Seas are particularly sensitive to long-term change and low-frequency modes of atmosphere-ocean-sea-ice forcing. The cold, low salinity surface waters of the Canada Basin of the Arctic Ocean are undersaturated with respect to CO<sub>2</sub> in the atmosphere and the region has the potential to take up atmospheric CO<sub>2</sub>, although presently suppressed by sea-ice cover. Undersaturated seawater CO<sub>2</sub> conditions of the Arctic Ocean are maintained by export of water with low dissolved inorganic carbon content and modified by intense seasonal shelf primary production. Sea-ice extent and volume in the Arctic Ocean has decreased over the last few decades, and we estimate that the Arctic Ocean sink for CO<sub>2</sub> has tripled over the last 3 decades (24 Tg yr<sup>-1</sup> to 66 Tg yr<sup>-1</sup>) due to sea-ice retreat with future sea-ice melting enhancing air-to-sea CO<sub>2</sub> flux by ~28% per decade. **Citation:** Bates, N. R., S. B. Moran, D. A. Hansell, and J. T. Mathis (2006), An increasing CO<sub>2</sub> sink in the Arctic Ocean due to sea-ice loss, *Geophys. Res. Lett.*, 33, L23609, doi:10.1029/2006GL027028.

### 1. Introduction

[2] The polar continental shelves are an active interface for the terrestrial, oceanic and atmospheric components of the Earth's biogeochemical system. Physical transformations and seasonal sea-ice dynamics play a major role in modifying the water-masses, ecosystems and the carbon cycle on the Chukchi Sea shelf, the western part of the Beaufort Sea shelf, and adjacent Arctic Ocean. Approximately 0.8 Sv (10<sup>6</sup> m<sup>3</sup> s<sup>-1</sup>) of Pacific Ocean water from the sub-polar Bering Sea enters the Arctic Ocean region through the Bering Strait [Aagaard *et al.*, 1985; Roach *et al.*, 1995; Woodgate and Aagaard, 2005; Woodgate *et al.*, 2005], fanning out across the shallow (<50 m deep) and expansive shelf of the Chukchi Sea [Codispoti *et al.*, 2005] before flowing into the Canada Basin of the central Arctic Ocean (Figure 1). Major outflows from the Chukchi Sea shelf of ~0.1–0.3 Sv each occur through Herald Valley, Long Strait and Barrow Canyon [Woodgate and Aagaard, 2005]. During transit across the Chukchi Sea shelf, the physical and biogeochemical properties of these water-masses are highly modified due to seasonal light and temperature changes, seasonal sea-ice dynamics, and primary production. The preconditioning and transformations of carbon over the Chukchi Sea continental shelf (and

other polar shelves) impacts air-sea CO<sub>2</sub> gas exchange in the Arctic Ocean.

[3] A comprehensive physical and biological oceanography survey of the Chukchi Sea, western Beaufort Sea shelf, and the adjacent Canada Basin of the Arctic Ocean was conducted in 2002 to 2004 under the auspices of Western Arctic Shelf-Basin Interactions (SBI) project [Grebmeier and Harvey, 2005; Codispoti *et al.*, 2005; Bates *et al.*, 2005a]. The SBI project provided opportunities to determine dissolved inorganic carbon (DIC), alkalinity (TA) and seawater partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) distributions and CO<sub>2</sub> dynamics on the continental shelf and Arctic Ocean during “winter/springtime” sea-ice covered periods and during the “summertime” peak period of seasonal sea-ice melt and retraction toward the pole.

### 2. Data and Methods

[4] As part of the hydrographic and biogeochemical sampling of the SBI project, water-column DIC and alkalinity samples were collected from the icebreaker USCGC *Healy* in 2002 and 2004 at numerous CTD stations across the Chukchi Sea and Canada Basin (Figure 1) of the Arctic Ocean. Two cruises sampled during the sea-ice covered, “winter/springtime” period [HLY02-01, 8 May–12 June 2002; HLY04-02; 15 May–23 June 2004]. In addition, there were two “summertime” cruises [cruise HLY02-03, 16 July–26 August 2002; HLY04-02; 17 July–26 August 2002] and one late-summer cruise [HLY04-04; 1 September–30 September 2004] during the sea-ice minima period.

#### 2.1. Calculation of Seawater pCO<sub>2</sub>

[5] Seawater pCO<sub>2</sub> concentrations were calculated from DIC and TA [Bates *et al.*, 2005a; Bates, 2006], and temperature and salinity data [http://catalog.eol.ucar.edu/sbi/]. Here, the carbonic acid dissociation constants of Mehrbach *et al.* [1973], as refit by Dickson and Millero, [1987] were used to determine seawater pCO<sub>2</sub> (see auxiliary materials)<sup>1</sup> [Bates, 2006]. The majority of samples from the Chukchi Sea and Canada Basin were collected from waters with a temperature range of ~-1.8°C to 0°C, and computed seawater pCO<sub>2</sub> had an average difference of ~2.5 μatm for different carbonic acid dissociation constants [Bates, 2006].

#### 2.2. Determination of Air-Sea CO<sub>2</sub> Flux

[6] The net air-sea CO<sub>2</sub> flux ( $F$ ) was determined by the following formula [ $F = k\sigma(\Delta p\text{CO}_2)$ ] where  $k$  is the transfer velocity,  $\sigma$  is the solubility of CO<sub>2</sub> and,  $\Delta p\text{CO}_2$  is the difference between atmospheric and oceanic partial pres-

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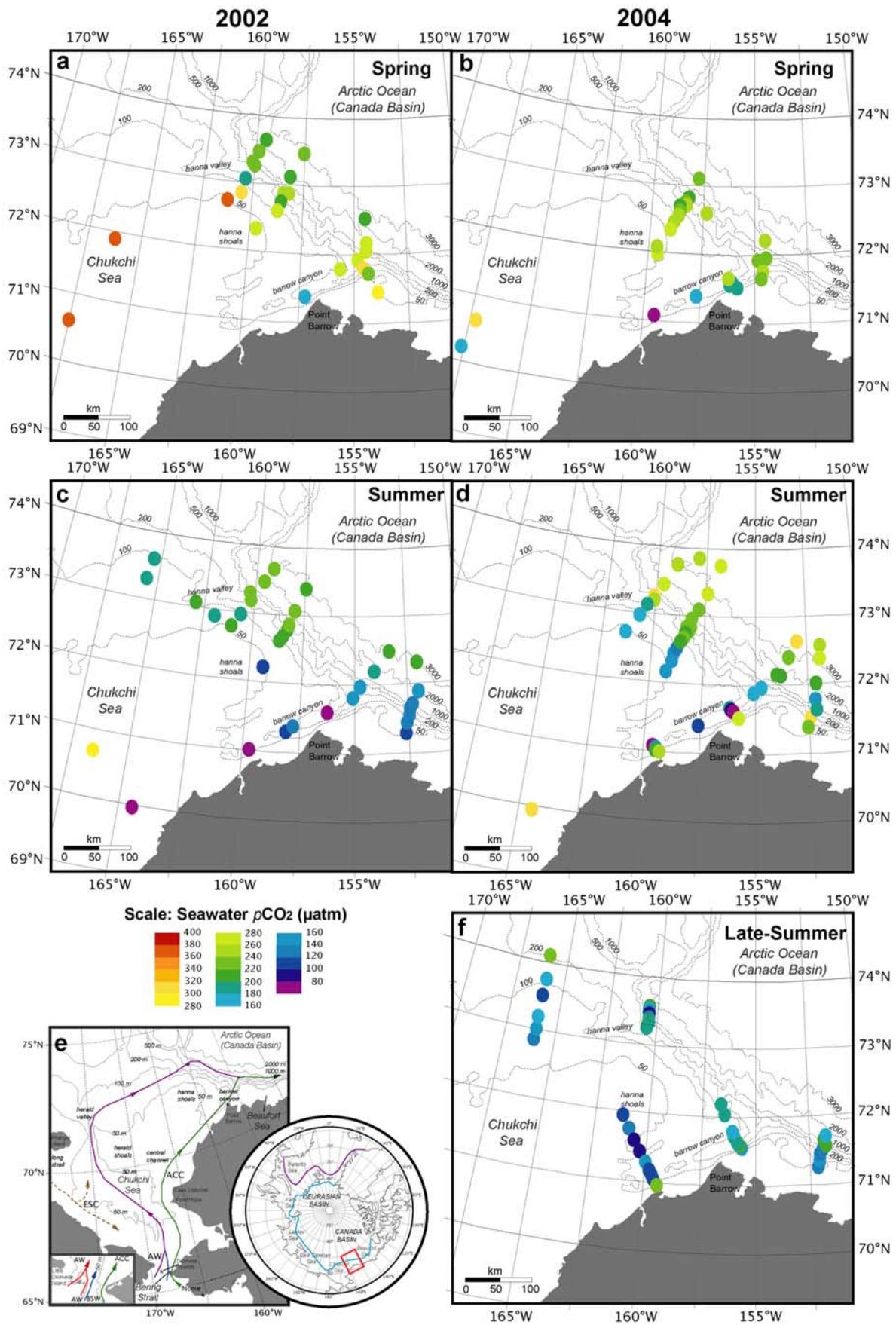


Figure 1

tures of CO<sub>2</sub>. The  $\Delta p\text{CO}_2$ , or air-sea CO<sub>2</sub> disequilibrium, sets the direction of CO<sub>2</sub> gas exchange while  $k$  determines the rate of air-sea CO<sub>2</sub> transfer. Gas transfer velocity-wind speed relationships for short-term wind conditions based on a quadratic ( $U^2$ ) dependency [Wanninkhof, 1992] between wind speed and  $k$  were used to determine air-sea CO<sub>2</sub> fluxes (see auxiliary materials for details). Atmospheric  $p\text{CO}_2$  data from Point Barrow in Alaska (<http://www.cmdl.noaa.gov>) and seawater  $p\text{CO}_2$  data from each CTD station were used to compute  $\Delta p\text{CO}_2$  values. Wind speed data (i.e., daily averages from 6-hourly observations) from the NCEP (National Center for Environmental Prediction)/NCAR (National Center for Atmospheric Research) reanalysis 2 data assimilation model (i.e., NNR data, <http://www.cdc.noaa.gov/cdc/data.ncep.html>) were used rather than shipboard observations to calculate  $k$  values. The spatial resolution of NNR data is 2.5° by 2.5° for the region of interest (i.e., 70°N–75°N; 165°W–150°W).

[7] The sea-ice barrier to gas exchange was accounted for by correcting air-sea CO<sub>2</sub> fluxes to the observed sea-ice conditions (data from SBI shipboard reports and satellite data; <http://catalog.eol.ucar.edu/sbi/>). For example, with sea-ice coverage conditions of 95%, 50%, and 0%, multipliers of 0.05, 0.5 and 1.00, respectively, were applied to calculation of  $F$ . In those regions with 100% sea-ice coverage, air-sea CO<sub>2</sub> gas exchange can occur through leads and fractures in the ice, and also potentially through sea-ice [Semiletov *et al.*, 2004]. In these regions, a multiplier of 0.01 (equivalent to 99% sea-ice cover) was used to allow for minor rates of air-sea CO<sub>2</sub> exchange through leads, fractures and brine channels.

### 3. Results and Discussion

#### 3.1. Chukchi Sea $p\text{CO}_2$ Distributions and Air-Sea CO<sub>2</sub> Fluxes

[8] Large seasonal winter/springtime to summertime changes in seawater  $p\text{CO}_2$  distributions were observed on the Chukchi Sea shelf adjacent to the Canada Basin. In the spring of 2002 and 2004, during sea-ice covered conditions, surface layer seawater  $p\text{CO}_2$  concentrations were undersaturated across the Chukchi Sea shelf (Figures 1a and 1b). At the Chukchi Sea shelf edge (i.e., water depth <200 m), seawater  $p\text{CO}_2$  values ranged from  $\sim 200$ – $280 \mu\text{atm}$  ( $\Delta p\text{CO}_2$  of  $\sim -100$ – $180 \mu\text{atm}$ ) with very low seawater  $p\text{CO}_2$  values (<100  $\mu\text{atm}$ ;  $\Delta p\text{CO}_2$  of >280  $\mu\text{atm}$ ) observed in the region of the Barrow Canyon polynya. Although

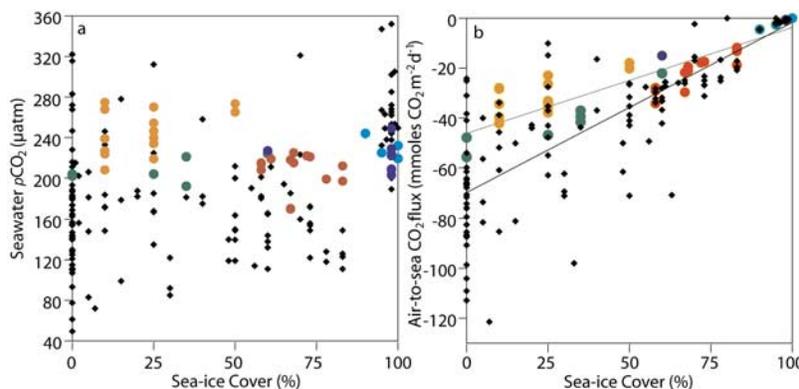
mixed layer waters were undersaturated with respect to atmospheric CO<sub>2</sub>, the influx of CO<sub>2</sub> to the ocean through air-sea gas exchange was low (<4 mmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup>), due primarily to suppression by sea-ice cover ( $\sim 95$ – $100\%$ ) [Bates, 2006].

[9] By mid-summer, sea-ice had retreated from Bering Strait northwards to the margins of the Canada Basin (Figures 1c and 1d). Across much of the Chukchi Sea, the brief exposure of nutrient laden surface layer (0– $\sim 30$  m) waters of Pacific origin flowing northward from Bering Strait over the sea-ice free Chukchi Sea shelf led to an intense seasonal bloom of phytoplankton [Cota *et al.*, 1996; Hill and Cota, 2005]. In the region of highest primary production, where there was complete exhaustion of inorganic nutrients, removal of DIC [Bates *et al.*, 2005a] and organic carbon [Bates *et al.*, 2005b; Moran *et al.*, 2005] from the surface waters, very low seawater  $p\text{CO}_2$  conditions were observed (<120–, 180  $\mu\text{atm}$ ) in 2002 and 2004 (Figures 1 and 2a). Extremely low seawater  $p\text{CO}_2$  values (<80  $\mu\text{atm}$ ;  $\Delta p\text{CO}_2$  of >300  $\mu\text{atm}$ ) were observed in Barrow Canyon (Figures 1c and 1d), through which the northern outflow of Chukchi Sea shelf waters are funneled (Figure 1e). By late summertime in 2004, seawater  $p\text{CO}_2$  conditions remained low (<100–160  $\mu\text{atm}$ ) prior to seasonal sea-ice advance (Figure 1f).

[10] During the sea-ice free period, surface waters of the Chukchi Sea were highly undersaturated with respect to atmospheric CO<sub>2</sub> ( $\Delta p\text{CO}_2$  of  $\sim >200$ – $300 \mu\text{atm}$ ), and the region acted seasonally as a very strong sink for atmospheric CO<sub>2</sub>. Air-to-sea CO<sub>2</sub> fluxes (computed with either NNR data or synoptic shipboard observations of wind-speed) had a median value of  $\sim 50$  mmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> (for sea-ice conditions of <5%; see Figure 2b and auxiliary materials Figure S1), with higher values (>120 mmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup>) in some regions of the Chukchi Sea. The mean air-to-sea CO<sub>2</sub> fluxes on the Chukchi Sea shelf for summer 2002, summer 2004, and late summer 2004 were  $36 \pm 25$  mmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup>,  $53 \pm 27$  mmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup>, and  $61 \pm 19$  mmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup>, respectively.

[11] Our estimates of mean air-to-sea CO<sub>2</sub> flux for the Chukchi Sea were three times higher than previous estimates of Kaltin and Anderson [2005], who used a simple carbon budget to indirectly estimate air-sea CO<sub>2</sub> fluxes. In their method, air-to-sea CO<sub>2</sub> flux was computed from the difference in DIC inventories (from very limited data) of waters flowing northward through Bering Strait and at the Chukchi Sea shelf edge, accounting for photosynthetic

**Figure 1.** Distributions of seawater  $p\text{CO}_2$  in the Chukchi Sea and Canada Basin. (a) Spring 2002 surface distributions of seawater  $p\text{CO}_2$  ( $\mu\text{atm}$ ) (HLY-02-01 cruise; 5 May–15 June 2002). (b) Spring 2004 surface distributions of seawater  $p\text{CO}_2$  ( $\mu\text{atm}$ ) (HLY-04-02 cruise; 17 May–21 June 2004). (c) Summer 2002 surface distributions of seawater  $p\text{CO}_2$  ( $\mu\text{atm}$ ) (HLY-02-03 cruise; 17 July–26 August 2002). (d) Summer 2004 surface distributions of seawater  $p\text{CO}_2$  ( $\mu\text{atm}$ ) (HLY-04-03 cruise; 16 July–26 August 2002). (e) Water mass circulation of the Chukchi Sea, western Beaufort Sea, and adjacent Arctic Ocean. Generalized circulation flows are shown. Water transiting through Bering Strait is composed of warmer, fresher Alaskan Coastal Current (ACC; green) waters in the east [Woodgate and Aagaard, 2005], Bering Shelf Water (BSW; blue) in central Bering Strait and colder, saltier, more nutrient-rich Anadyr Water (AW; red) to the west. Bering Shelf and Anadyr water merge into Bering Sea water (purple) within the Chukchi Sea [Roach *et al.*, 1995; Woodgate and Aagaard, 2005]. East Siberian Current (ESC) water intermittently flows into the Chukchi Sea from the west through Long Strait. (inset) Map of the Arctic Ocean with locations of Chukchi Sea, Beaufort Sea, and Canada Basin. Minimum summertime (cyan) and maximum wintertime (purple) sea-ice extent taken from 1972–2002 SSM/I data. (f) Late-summer 2004 surface distributions of seawater  $p\text{CO}_2$  ( $\mu\text{atm}$ ) (HLY-04-04 cruise; 1 September–30 September 2004). Contours (dashed brown line) indicate approximate distributions of sea-ice cover from SBI shipboard reports.



**Figure 2.** (a) Seawater  $p\text{CO}_2$  ( $\mu\text{atm}$ ) against sea-ice cover (%) from the Chukchi Sea (closed diamond symbol) and Canada Basin. (b) Air-to-sea  $\text{CO}_2$  flux ( $\text{mmoles CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ ) estimated for the Chukchi Sea (closed diamond symbol) and Canada Basin. Canada Basin data include: “winter/springtime” cruises (HLY02-01, 8 May–12 June 2002, blue symbol; HLY04-02, 15 May–23 June 2004, cyan symbol), and “summertime” cruises (HLY02-01, 8 May–12 June 2002, red symbol; HLY04-02, 15 May–23 June 2002, orange symbol; HLY04-04, 1 September–30 September 2004, green symbol).

uptake of  $\text{CO}_2$  as new production (from inorganic nutrient changes). The SBI observations indicate that the DIC content of surface and upper halocline winter/springtime waters across the Chukchi Sea and at Bering Strait (particularly in Alaskan Coastal Current water) were higher by  $>100 \mu\text{moles kg}^{-1}$  [Bates *et al.*, 2005a; Bates, 2006] compared to *Kaltin and Anderson* [2005]. In addition, the DIC of surface water outflowing the Chukchi Sea through Barrow Canyon (and Hanna Valley) [Bates *et al.*, 2005a; Bates, 2006] was much lower than observed by *Anderson and Kaltin* [2001] near the Chukchi Cap.

### 3.2. Canada Basin $p\text{CO}_2$ Distributions and Air-Sea $\text{CO}_2$ Fluxes

[12] At sampling stations in the Canada Basin of the Arctic Ocean (here defined as deeper than 200 m bottom depth), surface waters of the Polar Mixed Layer (PML; upper 30–50 m) were cold ( $\sim -0.5$  to  $-1.7^\circ\text{C}$ ) during winter/springtime, with a slightly warmer range ( $\sim +2$  to  $-1.7^\circ\text{C}$ ) during summertime. Seawater  $p\text{CO}_2$  contents had a small range ( $\sim 200$ – $270 \mu\text{atm}$ ; Figures 1 and 2a) and the average seawater  $p\text{CO}_2$  value for the PML was  $225 \pm 22 \mu\text{atm}$ . Surface layer seawater  $p\text{CO}_2$  showed little seasonal change between periods of high sea-ice cover (winter/springtime) and sea-ice minima conditions during summertime (Figure 2a). Furthermore, the average temperature corrected seawater  $p\text{CO}_2$  for PML water was  $224 \pm 27 \mu\text{atm}$  with little seasonal change (see auxiliary materials Figure S2). In order to account for seasonal temperature change in the PML, seawater  $p\text{CO}_2$  was corrected to a constant temperature of  $0^\circ\text{C}$  using the thermodynamic equation of 4.21% change in  $p\text{CO}_2$  per  $^\circ\text{C}$  change [Takahashi *et al.*, 1993]. Previous surveys along the sea-ice edge of the Chukchi and Beaufort Seas ( $\sim 150$ – $160^\circ\text{W}$ ,  $72$ – $74^\circ\text{N}$ ) in September also showed low seawater  $p\text{CO}_2$  conditions of  $\sim 160$ – $280 \mu\text{atm}$  [Pipko *et al.*, 2002; Murata and Takizawa, 2003]. Taken together, these observations suggest that the sea-ice covered surface waters of the Arctic Ocean (specifically the Canada Basin) remain perennially undersaturated with respect to  $\text{CO}_2$  in the atmosphere [Bates, 2006].

[13] Our observations indicate that the average  $\Delta p\text{CO}_2$  of PML waters in the Canada Basin was  $\sim 150 \pm 25 \mu\text{atm}$ . Although surface waters of the Canada Basin (and Arctic Ocean) were highly undersaturated and potentially a sink for atmospheric  $\text{CO}_2$ , the presence of sea-ice suppressed the rates of air-to-sea  $\text{CO}_2$  flux. For example, in the spring of 2002 and 2004, sea-ice cover at stations in the Canada Basin ranged from  $\sim 95\%$  to  $100\%$ , and air-to-sea  $\text{CO}_2$  fluxes were generally very low ( $<3 \text{ mmoles CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ ; Figure 2b) compared to the seasonally sea-ice free regions of the adjacent Chukchi and Beaufort Sea shelves (Figure 1). During summertime, sea-ice cover in the PML of the Canada Basin ranged from  $\sim 0\%$  to  $90\%$  and average air-to-sea  $\text{CO}_2$  fluxes were higher at  $\sim 55 \text{ mmoles CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ .

### 3.3. What Maintains $\text{CO}_2$ Undersaturation in the Canada Basin?

[14] Our observations of seawater  $p\text{CO}_2$  in Canada Basin indicate that the Arctic Ocean has a strong potential to be a sink for atmospheric  $\text{CO}_2$ , although, at present, suppressed by perennial sea-ice cover. Since sea-ice extent and volume in the Arctic Ocean has decreased over the last few decades [Cavaliere *et al.*, 2003; Rothrock and Zhang, 2005; Stroeve *et al.*, 2005; Wang *et al.*, 2005; Overland and Wang, 2005], and expected to decrease further over the next few decades, it is important to determine what maintains the seawater undersaturation of  $\text{CO}_2$  in the Arctic Ocean and if the  $\text{CO}_2$  sink in the Arctic Ocean region will change in the future.

[15] A major determinant of seawater  $p\text{CO}_2$  undersaturation in the Arctic Ocean is the physical and biogeochemical preconditioning upstream on the Chukchi and Beaufort Sea shelves. During summertime, the shelf to basin outflow of water from the Chukchi Sea shelf horizontally exports into the Canada Basin warm, biogeochemically modified surface water with a DIC deficit, and low seawater  $p\text{CO}_2$  ( $<200 \mu\text{atm}$ ) content due to intense shelf primary and net community production (NCP) [Hill and Cota, 2005; Bates *et al.*, 2005b]. Another contributor is a solubility effect on seawater  $\text{CO}_2$ , since surface layer waters cool by  $\sim 0.5$ – $1.5^\circ\text{C}$  during northward transit

across the Chukchi Sea shelf, decreasing seawater  $p\text{CO}_2$  at rate of  $\sim 4.21\%$  per  $^\circ\text{C}$  [Takahashi *et al.*, 1993]. At other times during the year, the continual northward flow of water also exports waters undersaturated with respect to the atmospheric CO<sub>2</sub> (seawater  $p\text{CO}_2$  at 300–350  $\mu\text{atm}$ ) [Bates, 2006]. The Arctic Ocean is also significantly impacted by freshwater inputs from rivers. Recent estimates suggest that approximately 8 m of the upper 40 m of the Canada Basin surface layer has freshwater origins [Macdonald *et al.*, 2002], potentially bringing excess alkalinity into the Arctic Ocean.

[16] These physical and biogeochemical factors combine to enhance the capacity of the Arctic Ocean surface layer to absorb CO<sub>2</sub>. The capacity of seawater to absorb CO<sub>2</sub> depends primarily on the buffer capacity or Revelle Factor of seawater [Takahashi *et al.*, 1993; Sabine *et al.*, 2004]. The Revelle Factor quantifies the rate of change of  $p\text{CO}_2$  to dissolved inorganic carbon (DIC) in water masses and reflects the underlying seawater charge balance and, importantly, the ratio of DIC to alkalinity. Tropical and subtropical waters tend to have low Revelle Factors (8–10) with a greater capacity to absorb atmospheric CO<sub>2</sub> compared to temperate and sub-polar waters with high Revelle Factors (11–14). Recent studies [Bates, 2006] indicate that the surface waters of the Canada Basin have unusually low Revelle Factors ( $\sim 3.5$ – $6.5$ ) due to the removal of DIC (while alkalinity remains unchanged) on the Chukchi Sea shelf by NCP. The addition of river alkalinity that act to decrease the DIC:TA ratio (shifting waters to lower Revelle Factors) of Arctic Ocean surface waters [Bates, 2006].

[17] All these factors have a strong preconditioning influence due to the relatively short residence time of Arctic Ocean surface waters. The residence time of surface layer waters of the Canada Basin has been estimated at  $\sim 15$  years [Hansell *et al.*, 2004], and shorter ( $< 10$  years) in the Eurasian Basin [Anderson and Kaltin, 2001] due to export out of the Fram Strait. Given the volume of polar mixed layer waters in the Arctic Ocean ( $\sim 2.9 \times 10^{14}$  m<sup>3</sup>), the upper 50 m of the Arctic Ocean has a turnover rate of  $\sim 10$  years due to the northward ( $\sim 0.8$  Sv) flow of Pacific Ocean waters through Bering Strait.

### 3.4. Future Changes in the Arctic Ocean CO<sub>2</sub> Sink

[18] How will the CO<sub>2</sub> sink in the Arctic Ocean region potentially change in the future? Past studies [Anderson *et al.*, 1998] have estimated the annual net air-to-sea CO<sub>2</sub> flux over the Arctic Ocean and adjacent continental shelves to be  $\sim 24$  Tg C year<sup>-1</sup>. However, recent estimates suggest that the Chukchi Sea and entire Arctic Ocean (including the Chukchi Sea) is a larger net oceanic sink for atmospheric CO<sub>2</sub> at  $\sim 38$  and 66 Tg C year<sup>-1</sup>, respectively [Bates, 2006]. During the last couple of decades, the rate of loss of sea-ice from the central Arctic Ocean is estimated at  $0.036 \times 10^6$  km year<sup>-1</sup> [Cavaliere *et al.*, 2003], approximately  $0.6\%$  year<sup>-1</sup> of the total surface area ( $5.8 \times 10^6$  km<sup>2</sup>) of the Arctic Ocean. The loss of sea-ice is expected to, both reduce the % sea-ice cover in the sea-ice marginal, zone and expose undersaturated waters the Arctic Ocean (i.e. Canada and Eurasian Basins). We expect air-to-sea CO<sub>2</sub> flux to increase relative to decreasing sea-ice % cover generally along the regression line shown in Figure 2b. Where PML waters of the Canada Basin are exposed during seasonally

sea-ice free conditions, the mean net air-to-sea CO<sub>2</sub> flux was  $\sim 46 \pm 8$  mmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> (i.e., intercept, at 0% sea-ice cover in Figure 2b). Scaling these observations from the Canada Basin to the entire Arctic Ocean region, we compute that the average annual loss of sea-ice enhances air-to-sea CO<sub>2</sub> flux (i.e.,  $\sim 0.55$  g CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup>; assuming sea-ice free conditions of  $\sim 100$  days year<sup>-1</sup>) into the Arctic Ocean by  $\sim 2.0 \pm 0.3$  Tg C year<sup>-1</sup>, with the effect compounding over time. Here, we only consider the effects, of sea-ice loss in the Arctic Ocean and not elsewhere in the marginal sea-ice zones (e.g., Bering Sea).

[19] The extent of Arctic Ocean sea-ice has declined by  $\sim 0.9 \times 10^6$  km over the last 30 years (1972–2002) [Cavaliere *et al.*, 2003]. At present, the net Arctic Ocean sink for atmospheric CO<sub>2</sub> has been estimated at  $\sim 66$  Tg C yr<sup>-1</sup> for 2002 [Bates, 2006]. However, using the air-to-sea CO<sub>2</sub> rate change of 2.0 Tg C yr<sup>-1</sup> due to sea-ice decrease, we compute that the Arctic Ocean sink for atmospheric CO<sub>2</sub> would have been smaller in 1972 at  $\sim 20$  Tg C yr<sup>-1</sup>, similar to the carbon budget estimates of Anderson *et al.* [1998]. Thus, from the late 1960's/early 1970's, the Arctic Ocean sink for atmospheric CO<sub>2</sub> may have tripled (from  $\sim 24$  to  $\sim 66$  Tg C yr<sup>-1</sup>) since the onset of sea-ice decline in the Arctic Ocean [e.g., Cavaliere *et al.*, 2003; Wang *et al.*, 2005; Overland and Wang, 2005; Rothrock and Zhang, 2005; Stroeve *et al.*, 2005]. Extrapolating our results into the future suggests that the net air-to-sea CO<sub>2</sub> flux will increase by  $\sim 20 \pm 3$  Tg C (or  $\sim 28 \pm 4\%$  by the year 2012 assuming that 2002 is used as a starting point) in the next decade. If all the sea-ice of the Arctic Ocean melted (assuming surface layer  $p\text{CO}_2$  of  $\sim 225 \pm 25$   $\mu\text{atm}$  and similar seasonal distribution of wind in the Canada Basin as the adjacent Chukchi Sea slope), there would be a one-time uptake of  $\sim 1.2 \pm 0.2$  Pg C ( $10^{15}$  g C). This compares to a previous estimate of 0.28 Pg C [Anderson and Kaltin, 2001] who computed how much CO<sub>2</sub> was needed to equilibrate the PML with the atmosphere using data from the Eurasian Basin. If we use a similar approach using vertical profiles of DIC observed in the Canada Basin from 2002 to 2004, we estimate the uptake required would be  $\sim 1.86 \pm 0.2$  Pg C (see auxiliary materials for details). The difference in estimates presumably reflects differences in the vertical distribution of DIC between the Canada Basin and Eurasian Basin.

[20] This future projection of the Arctic Ocean CO<sub>2</sub> sink could be counteracted or enhanced by other mechanisms. Warming associated with melting of sea-ice in the Arctic Ocean basin should conservatively increase surface temperatures ( $\sim 1.8^\circ\text{C}$  to  $> 0^\circ\text{C}$ ) and seawater  $p\text{CO}_2$  by  $\sim 25$ – $30$   $\mu\text{atm}$ , thereby lowering the compounding annual enhancement of net air-to-sea CO<sub>2</sub> flux from ice retreat by  $\sim 20\%$  (i.e., 2.0 to 1.6 Tg C year<sup>-1</sup>). We assume that melting of sea-ice dilutes DIC and alkalinity with negligible impact on seawater  $p\text{CO}_2$ . Freezing and brine formation might also slightly enhance the air-to-sea CO<sub>2</sub> flux [Anderson *et al.*, 2004]. Other studies have suggested that the melting of sea-ice might enhance primary production and the Arctic Ocean CO<sub>2</sub> sink [Anderson and Kaltin, 2001]. However, given the very low nitrate and phosphate concentrations observed in the Arctic Ocean [Codispoti *et al.*, 2005], we anticipate a minor enhancement of the vertical C flux ( $\sim 0.03$  Tg C year<sup>-1</sup>) out of the surface

layer (assuming a NO<sub>3</sub> content of 0.2 μmoles kg<sup>-1</sup> and mixed layer of 50 m).

[21] Processes that can contribute to the budget of CO<sub>2</sub> in the PML include vertical diffusion, primary production, downwelling, gas exchange, and lateral transport. At present, the gain of DIC (and increase in pCO<sub>2</sub>) in the PML due to the upward diffusion of CO<sub>2</sub> from the underlying upper halocline layer appears to roughly balance the loss of CO<sub>2</sub> due to downwelling of the PML and export of organic carbon due to phytoplankton primary production (see auxiliary materials<sup>1</sup> for details). The upward vertical diffusional flux of CO<sub>2</sub> was estimated from very low vertical eddy diffusivity reported by Wallace *et al.* [1987] ( $2 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ ) or calculated from SBI temperature and salinity profiles [ $1.4 \pm 1.0 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ ]. The loss of CO<sub>2</sub> from the PML of the Canada Basin due to downwelling was estimated assuming a downwelling term of 0.5 m yr<sup>-1</sup> [Wallace *et al.*, 1987]. Finally, the loss of CO<sub>2</sub> from the PML due to primary production was estimated from low estimates of annual primary production in the central Arctic Ocean ( $\sim 0.6\text{--}1.3 \text{ g C m}^{-2} \text{ year}^{-1}$  [Anderson *et al.*, 2003];  $1.8 \text{ g C m}^{-2} \text{ year}^{-1}$  [English, 1961];  $3.6 \text{ g C m}^{-2} \text{ year}^{-1}$  [Moran *et al.*, 1997]) or estimates of net community production from the Canada Basin (e.g.,  $2.2\text{--}6.5 \text{ g C m}^{-2} \text{ year}^{-1}$  [Bates *et al.*, 2005a]). Any significant change in the balance of these and other processes could lead to changes in the seawater pCO<sub>2</sub> undersaturation and potential CO<sub>2</sub> sink observed in the Canada Basin (and Eurasian Basin).

[22] If there were any change in the transport of inorganic nutrients to the surface layer of the Arctic Ocean basin, this may impact the rate of air-sea CO<sub>2</sub> flux. At present, the inorganic nutrients of surface waters transiting northward across the shelf during the summertime ( $\sim 100$  days duration) are consumed by the time they reach the deep basin [Codispoti *et al.*, 2005]. During the other times of the year ( $\sim 270$  days), we estimate that an outflow of surface water (with nitrate concentrations of  $\sim 15 \text{ μmoles kg}^{-1}$ ) of 0.4 Sv from the Chukchi Sea shelf could enhance the rate of primary production in the Arctic Ocean by  $\sim 10 \text{ Tg C year}^{-1}$ , or  $\sim 1.7 \text{ g C m}^{-2} \text{ year}^{-1}$ . This compares to the enhancement of primary production of  $17 \text{ Tg C year}^{-1}$  for water flowing into the Arctic Ocean from the Barents Sea [Anderson and Kaitin, 2001].

[23] Over the next 10 year period (e.g., 2002 to 2012), the surface layer could potentially absorb an extra  $\sim 100 \text{ Tg C}$  (i.e.,  $\sim 2.0 \text{ Tg C year}^{-1}$  compounded each year) due to continued reduction of Arctic Ocean sea-ice. Since the average polar mixed layer depth is  $\sim 50 \text{ m}$ , we would expect seawater DIC and pCO<sub>2</sub> contents to increase by  $\sim 24 \text{ μmoles kg}^{-1}$  and  $\sim 30 \text{ μatm}$ , respectively over a 10 year period. The increase in seawater pCO<sub>2</sub> would thus reduce the ocean CO<sub>2</sub> sink enhancement by  $\sim 20\%$  (this assumes that the rate of sea-ice loss continues at previous rates, and that other potential factors such as Arctic Ocean basin primary production and export, Chukchi Shelf transport of freshwater, nutrients, DIC, organic matter, and alkalinity remain unchanged). But, given the relatively short residence times ( $\sim 15$  years) of Arctic Ocean surface water, continued inputs of shelf water would dilute the DIC accumulation due to enhanced air-to-sea CO<sub>2</sub> flux. Furthermore, if the freshwater input of alkalinity to the Arctic

Ocean by rivers increases in the future, this contribution may sustain the low Revelle Factor and the high capacity of surface water to absorb CO<sub>2</sub>. Considering all factors, we anticipate that the oceanic sink of CO<sub>2</sub> in Arctic Ocean will continue to increase for a period related to the future duration of the sea-ice loss from the Arctic Ocean.

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## References

- Aagaard, K., J. H. Swift, and E. C. Carmack (1985), Thermohaline circulation in the Arctic Mediterranean seas, *J. Geophys. Res.*, **95**, 18,163–18,175.
- Anderson, L. G., and S. Kaitin (2001), Carbon fluxes in the Arctic Ocean—Potential impact by climate change, *Polar Res.*, **20**(2), 225–232.
- Anderson, L. G., K. Olsson, and M. Chierici (1998), A carbon budget for the Arctic Ocean: Inventory and sinks, *Global Biogeochem. Cycles*, **12**, 455–465.
- Anderson, L. G., E. P. Jones, and J. H. Swift (2003), Export production in the central Arctic Ocean evaluated from phosphate deficits, *J. Geophys. Res.*, **108**(C6), 3199, doi:10.1029/2001JC001057.
- Anderson, L. G., E. Falck, E. P. Jones, S. Jutterström, and J. H. Swift (2004), Enhanced uptake of atmospheric CO<sub>2</sub> during freezing of seawater: A field study in Storfjorden, Svalbard, *J. Geophys. Res.*, **109**, C06004, doi:10.1029/2003JC002120.
- Bates, N. R. (2006), Air-sea CO<sub>2</sub> fluxes and the continental shelf pump of carbon in the Chukchi Sea adjacent to the Arctic Ocean, *J. Geophys. Res.*, **111**, C10013, doi:10.1029/2005JC003083.
- Bates, N. R., M. H. P. Best, and D. A. Hansell (2005a), Spatio-temporal distribution of dissolved inorganic carbon and net community production in the Chukchi and Beaufort Seas, *Deep Sea Res., Part II*, **52**, 3303–3323.
- Bates, N. R., D. A. Hansell, S. B. Moran, and L. A. Codispoti (2005b), Seasonal and spatial distributions of particulate organic matter (POM) in the Chukchi Sea, *Deep Sea Res., Part II*, **52**, 3324–3343.
- Cavaliere, D. J., C. L. Parkinson, and K. Y. Vinnikov (2003), 30-Year satellite record reveals contrasting Arctic and Antarctic decadal sea ice variability, *Geophys. Res. Lett.*, **30**(18), 1970, doi:10.1029/2003GL018031.
- Codispoti, L. A., C. Flagg, and V. Kelly (2005), Hydrographic conditions during the 2002 SBI process experiments, *Deep Sea Res., Part II*, **52**, 3199–3226.
- Cota, G. F., L. R. Pomeroy, W. G. Harrison, E. P. Jones, F. Peters, W. M. Sheldon, and T. R. Weingartner (1996), Nutrients, primary production and microbial heterotrophy in the southeastern Chukchi Sea: Arctic summer nutrient depletion and heterotrophy, *Mar. Ecol. Prog. Ser.*, **135**(1–3), 247–258.
- Dickson, A. G., and F. J. Millero (1987), A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media, *Deep Sea Res.*, **34**, 1733–1743.
- English, T. S. (1961), Some biological oceanographic observations in the central north Polar Sea, Drift Station Alpha, 1957–1958, *Arct. Inst. of N. Am., Sci. Rep.*, **15**, Calgary, Alberta, Canada.
- Grebmeier, J. M., and H. R. Harvey (2005), The western Arctic Shelf-basin Interactions (SBI) project. An overview, *Deep Sea Res., Part II*, **52**, 3109–3115.
- Hansell, D. A., D. Kadko, and N. R. Bates (2004), Degradation of terrigenous dissolved organic carbon in the western Arctic Ocean, *Science*, **304**, 858–861.
- Hill, V. J., and G. F. Cota (2005), Spatial patterns of primary production in the Chukchi Sea in the spring and summer of 2002, *Deep Sea Res., Part II*, **52**, 3344–3354.
- Kaitin, S., and L. G. Anderson (2005), Uptake of atmospheric carbon dioxide in Arctic shelf seas: Evaluation of the relative importance of processes that influence pCO<sub>2</sub> in water transported over the Bering-Chukchi Sea shelf, *Mar. Chem.*, **94**, 67–79.
- Macdonald, R. W., F. A. McLaughlin, and E. C. Carmack (2002), Fresh water and its sources during the SHEBA drift in the Canada Basin of the Arctic Ocean, *Deep Sea Res., Part I*, **49**, 1769–1785.

- Mehrbach, C., C. H. Culbertson, J. E. Hawley, and R. M. Pytkowicz (1973), Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, *Limnol. Oceanogr.*, *18*, 897–907.
- Moran, S. B., K. M. Ellis, and J. N. Smith (1997), <sup>234</sup>Th/<sup>238</sup>U disequilibrium in the central Arctic Ocean: Implications for particulate organic carbon export, *Deep Sea Res., Part II*, *44*, 1593–1606.
- Moran, S. B., et al. (2005), Seasonal changes in POC export flux in the Chukchi Sea and implications for water column-benthic coupling in Arctic shelves, *Deep Sea Res., Part II*, *52*, 3427–3451.
- Murata, A., and T. Takizawa (2003), Summertime CO<sub>2</sub> sinks in shelf and slope waters of the western Arctic Ocean, *Cont. Shelf Res.*, *23*(8), 753–776.
- Overland, J. E., and M. Wang (2005), The Arctic climate paradox: The recent decrease of the Arctic Oscillation, *Geophys. Res. Lett.*, *32*, L06701, doi:10.1029/2004GL021752.
- Pipko, I. I., I. P. Semiletov, P. Y. Tishchenko, S. P. Pugach, and J. P. Christensen (2002), Carbonate chemistry dynamics in Bering Strait and the Chukchi Sea, *Prog. Oceanogr.*, *55*(1–2), 77–94.
- Roach, A. T., K. Aagaard, C. H. Pease, S. A. Salo, T. J. Weingartner, V. Pavlov, and M. Kulakov (1995), Direct measurements of transport and water properties through Bering Strait, *J. Geophys. Res.*, *100*, 18,443–18,457.
- Rothrock, D. A., and J. Zhang (2005), Arctic Ocean sea ice volume: What explains its recent depletion?, *J. Geophys. Res.*, *110*, C01002, doi:10.1029/2004JC002282.
- Sabine, C. L., et al. (2004), The oceanic sink for anthropogenic CO<sub>2</sub>, *Science*, *305*, 367–371.
- Semiletov, I., A. Makshtas, S.-I. Akasofu, and E. L. Andreas (2004), Atmospheric CO<sub>2</sub> balance: The role of Arctic sea ice, *Geophys. Res. Lett.*, *31*, L05121, doi:10.1029/2003GL017996.
- Stroeve, J. C., M. C. Serreze, F. Fetterer, T. Arbetter, W. Meier, J. Maslanik, and K. Knowles (2005), Tracking the Arctic's shrinking ice cover: Another extreme September minimum in 2004, *Geophys. Res. Lett.*, *32*, L04501, doi:10.1029/2004GL021810.
- Takahashi, T., J. Olafsson, J. G. Goddard, D. W. Chipman, and S. C. Sutherland (1993), Seasonal variation of CO<sub>2</sub> and nutrients in the high-latitude surface oceans: A comparative study, *Global Biogeochem. Cycles*, *7*(40), 843–878.
- Wallace, D. W. R., B. Moore, and E. P. Jones (1987), Ventilation of the Arctic Ocean cold halocline: Rates of diapycnal and isopycnal transport, oxygen utilization, and primary production inferred using chlorofluoromethane distribution, *Deep Sea Res.*, *34*, 1957–1979.
- Wang, J., M. Ikeda, S. Zhang, and R. Gerdes (2005), Linking the Northern Hemisphere sea-ice reduction trend and the quasi-decadal arctic sea-ice oscillation, *Clim. Dyn.*, *24*, 115–130.
- Wanninkhof, R. (1992), Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, *97*, 7373–7382.
- Woodgate, R. A., and K. Aagaard (2005), Revising the Bering Strait freshwater flux into the Arctic Ocean, *Geophys. Res. Lett.*, *32*, L02602, doi:10.1029/2004GL021747.
- Woodgate, R. A., K. Aagaard, and T. J. Weingartner (2005), A year in the physical oceanography of the Chukchi Sea: Moored measurements from autumn 1990–1991, *Deep Sea Res., Part II*, *52*, 3116–3149.

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