Controls on the seasonal variability of calcium carbonate saturation states in the Atlantic gateway to the Arctic Ocean

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ABSTRACT

In addition to ocean acidification due to a gradual anthropogenic CO_2 uptake, strong seasonal variations in the carbonate system occur in the Arctic Ocean as a result of physical and biological processes. Understanding this seasonal variability is critical for predicting the onset of calcium carbonate mineral (Ω) undersaturation with increasing atmospheric CO_2 concentrations. However, these variations are currently poorly understood because of a lack of winter data due to the challenging field conditions in this season. Here we report observations over an annual cycle of the carbonate system of surface waters in the Atlantic gateway to the Arctic Ocean, covering the region between Svalbard and mainland Norway. Dissolved inorganic carbon (DIC) concentrations ranged from 2137–2148 μmol kg^{-1} in winter to 1986–2094 μmol kg^{-1} in summer, and total alkalinity (TA) concentrations between 2312–2341 μmol kg^{-1} in winter and 2199–2317 μmol kg^{-1} in summer. This resulted in an increase in TA:DIC ratios from 1.077–1.090 in winter to 1.106–1.112 in summer, mainly due to the biological uptake of CO_2 during spring and summer. Similarly, a significant seasonal variability was observed in Ω (0.4–0.9), with lowest saturation states in winter ($\Omega_{aragonite} \sim 1.8$–2.1) and highest in spring and summer ($\Omega_{aragonite} \approx 2.4$). Analysis of the biogeochemical and physical processes that impact aragonite saturation states (Ω_{ar}) showed biological production to be the most important factor driving seasonal variability in Ω_{ar} in this area, accounting for 45–70% of the difference between winter and summer values. Future changes in these processes may alter the seasonal cycle of the carbonate system in both amplitude and timing, and further observations are required to determine the progress of ocean acidification in the Atlantic waters entering the Arctic Ocean.

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1. Introduction

The addition of CO_2 to seawater results in well-known shifts in the oceanic carbonate system equilibria with the consumption of carbonate ions (CO_3^{2-}) resulting in the reduction of saturation states with respect to calcium carbonate minerals (Ω) and a decrease in pH (Zeebe and Wolf-Gladrow, 2001). The decrease in surface water pH due to the oceanic uptake of anthropogenic CO_2 has been predicted by models (Caldeira and Wickett, 2003) and reported from measurements in various ocean regions (Bates and Peters, 2007; Byrne et al., 2010; Santana-Casiano et al., 2007). For instance, saturation states in the Pacific Ocean have decreased by ca. 6% over the last two decades (Feely et al., 2012), corresponding to a lowering of the saturation state of aragonite (Ω_{ar}) from 3.6 to 3.4 off the coast of Japan (Ishii et al., 2011). Continuous decreases at this rate may have direct implications for calcifying organisms in the world's ocean (Feely et al., 2004).

High-latitude oceans have naturally higher CO_2 concentrations when compared to subtropical and tropical oceans due to the increased solubility of CO_2 at lower temperatures (Anderson and Smith, 2001; Fabry et al., 2009), resulting in lower Ω values and higher Revelle factors (decreased CO_2 buffering capacity). Polar oceans are thus naturally poised closer to calcium carbonate undersaturation (Sabine et al., 2004). The Arctic Ocean is particularly vulnerable to climate change with increased warming, rapidly declining sea-ice and increased river inputs reported over the last decades (Comiso et al., 2008; Holland, 2013; Markus et al., 2009; Peterson et al., 2002; Tank et al., 2012), resulting in potentially profound impacts on primary productivity (Arrigo et al., 2008, 2012), the biological carbon pump (Nishino et al., 2011), terrestrial carbon delivery and mineralization (Anderson et al., 2009), ecosystem functioning (Post et al., 2009) and sub-sea floor methane release (Westbrook et al., 2009). The progress of ocean acidification will be affected by the changes in air–sea CO_2 fluxes caused by these climate change induced processes (Arrigo et al., 2010; Jutterstrom and Anderson, 2010; Yamamoto et al., 2012) and corresponding feedbacks (McGuire et al., 2006; McNeil and Matear, 2007) as they alter the marine carbon cycle (Bates and Mathis, 2009; McGuire et al., 2009).

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Earlier studies on carbonate system biogeochemistry in the Arctic Ocean focused mainly on air–sea fluxes and carbon budgets (Anderson et al., 1990, 1998; Kaltin et al., 2002; Pipko et al., 2002; Yager et al., 1995). These efforts are still continuing (Bates et al., 2011; McNeil and Matear, 2007; Mucci et al., 2010; Pipko et al., 2011; Rysgaard et al., 2009; Schuster et al., 2013), with recent studies also reporting on the impacts on Ω of biological processes (Bates et al., 2009; Chierici et al., 2011), freshwater run-off (Chierici and Fransson, 2009; Yamamoto-Kawai et al., 2011), the continental shelf pump (Anderson et al., 2010), upwelling of undersaturated waters (Mathis et al., 2012) and lateral mixing (Azetsu-Scott et al., 2010). These recent efforts are a consequence of the recognition that the Arctic Ocean will be the first ocean region to experience widespread undersaturation of surface waters (Steinacher et al., 2009). Individual occurrences of aragonite undersaturation have already been observed in surface waters of the Canada Basin, Chukchi Sea, Canadian Arctic Archipelago and Beaufort Sea (Bates et al., 2009; Chierici and Fransson, 2009; Yamamoto-Kawai et al., 2009).

Superimposed on the gradual anthropogenically driven decrease of Ω are the natural seasonal variations of the carbonate system, driven by physical and biological processes, which over an annual cycle can be one or two orders of magnitude larger than the anthropogenic CO_2 facilitated decrease (Ishii et al., 2011). In the Southern Ocean, inclusion of seasonal variability brings forward the model-predicted date of first undersaturation by 30 years (McNeil and Matear, 2008). Comparison of a full annual cycle of the carbonate system in both polar oceans, suggests that the Arctic may be more vulnerable to ocean acidification than the Southern Ocean, due to a lower buffering capacity, larger temperature cycle and reduced nutrient availability (Shadwick et al., 2013). Strong seasonal changes occur in the Arctic as a result of temperature variations, ice-melt and formation, and biological productivity but little is known about the exact carbonate system dynamics due to these changes, partly due to the lack of winter observations for the Arctic, when the logistics of dealing with sea-ice and poor weather conditions make data collection challenging. In the Pacific sector of the Arctic

Ocean recent studies have included winter data and reported on the seasonal variations in pCO_2 (Else et al., 2012; Yager et al., 1995), dissolved inorganic carbon (DIC) (Shadwick et al., 2011) and Ω (Bates et al., 2009; Chierici et al., 2011; Mathis and Questel, 2013). In the Atlantic sector several studies have examined the seasonal variations in DIC (Miller et al., 1999; Skjelvan et al., 1999) and pCO_2 (Omar et al., 2007; Rysgaard et al., 2009), but so far no in depth reports exist on the seasonal variation of Ω. Recently Yakushev and Sorensen (2013), using observations and a modelling approach, examined the role of organic matter in the seasonality of the carbonate system at the entrance to the Barents Sea, and included a limited discussion of the seasonality of Ω.

We present surface water DIC and total alkalinity (TA) data collected during four seasons along a route between the Norwegian and Barents Seas, the main entry route of Atlantic water into the Arctic Ocean. The annual cycles of TA (Section 3.1) and DIC (Section 3.2) are described first, followed by the seasonality of Ω (Section 3.3) described in terms of TA:DIC ratios (Section 3.3.1). We examine the physical, chemical and biological processes driving the seasonal variability of the carbonate system and quantify the relative contribution of each process to the seasonal dynamics of Ω in this area (Section 3.3.2). The results are discussed from a Pan-Arctic point of view (Section 3.4) and the main implications for the findings identified (Section 3.5).

1.1. Hydrography and physical conditions

The study area is characterized by a shelf-break where several warm and cold water surface currents (Norwegian Coastal Current; Norwegian Atlantic Current; West Spitsbergen Current; West Spitsbergen Coastal Current) converge and diverge (Fig. 1), giving rise to a dynamic and variable hydrography (Furevik, 2001). The average depth along the transect was ca. 200 m, with maximum depths of ca. 400 m found south of Bear Island (Jakobsson, 2002).

Three hydrographic areas can be differentiated along the transect (Fig. 1): 1) Norwegian Coast, up to 71.5°N and dominated by the relatively fresh Norwegian Coastal Current (S < 34.7); 2) Barents
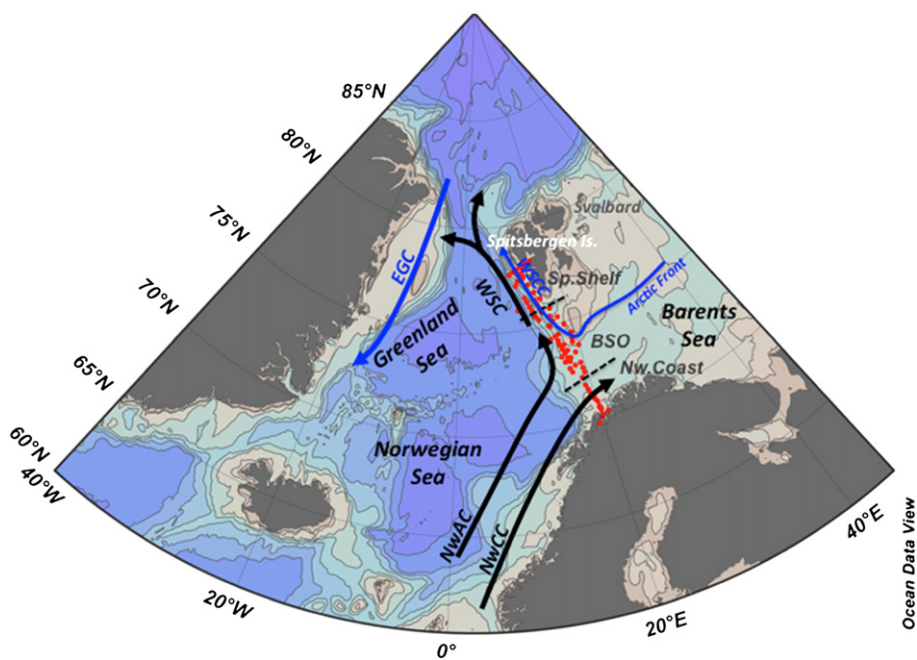
Fig. 1. Map showing the major surface currents in the study area. Warm, saltier currents are shown in black, and cold, fresher currents in blue. The Polar Front is shown as blue line. The sampling points along the Tromsø-Spitsbergen line are shown as red dots with the boundaries between the three hydrographic areas along the transect shown with dashed black lines. (EGC: East Greenland Current; NwAC: Norwegian Atlantic Current; NwCC: Norwegian Coastal Current; WSC: West Spitsbergen Current; WSSC: West Spitsbergen Coastal Current; Nw. Coast: Norwegian Coast; BSO: Barents Sea Opening; Sp. Shelf: Spitsbergen Shelf).