The State and Variability of the Carbonate System of the Canadian Arctic in the Context of Ocean Acidification

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Abstract

Ocean acidification is an important yet often disregarded outcome of the rise in atmospheric CO₂ levels. Roughly a third of the CO₂ released to the atmosphere since the industrial revolution has been absorbed by the world's oceans, resulting in a decrease in seawater pH, carbonate ion concentration and saturation state with respect to the calcium carbonate minerals aragonite and calcite (Ω_A , Ω_C). The Arctic Ocean is particularly vulnerable to acidification due to the weak buffer capacity of its cold waters and its steadily decreasing sea-ice cover. The ongoing changes in seawater chemistry constitute a potential threat for the health of marine ecosystems, particularly to calcifying organisms whose ability to secrete calcium carbonate skeletons and shells might be hindered by a decrease in pH and Ω .

Scientific interest towards ocean acidification and its effects on marine ecosystems of the Canadian Arctic Archipelago and its adjacent basins (Canada Basin and Baffin Bay) has grown over the last two decades, yet recent surveys of carbonate system parameters in the region are limited in scope and significant knowledge gaps remain. A vast dataset spanning 2003 – 2016 is used to characterize the recent state of the carbonate system in the Canadian Arctic, which is found to act as a net CO₂ sink in the summer and hosts two areas of consistent surface undersaturation with respect to aragonite, the central Canada Basin and the Queen Maud Gulf.

Discontinuous time series highlight the strong variability of carbonate system parameters in this dynamic region, where biological activity accounts for approximately a third of the variability in surface DIC. The ocean acidification signal is estimated to emerge from the natural variability of the system in time series of pH, pCO₂ and Ω_A spanning 20 to 30 years.

Résumé

Quoique méconnue du grand public, l'acidification des océans est une importante conséquence de la croissance de la concentration atmosphérique de dioxyde de carbone. Les océans ont absorbé environ le tiers du CO₂ émis par les activités humaines depuis l'industrialisation, causant une diminution du pH, de la concentration en ions carbonates et de la saturation de l'eau de mer par rapport aux minéraux de carbonate de calcium, l'aragonite et calcite (Ω_A , Ω_C). L'Océan Arctique est particulièrement vulnérable à ce phénomène dû à la faible capacité de ses eaux froides à tamponner leur pH, relativement aux eaux des autres océans, et à la diminution rapide de son couvert de glace. Les changements engendrés par l'acidification de l'eau de mer constituent une menace potentielle pour plusieurs organismes marins, particulièrement pour les organismes calcifiants dont les squelettes et coquilles sont constituées de carbonate de calcium (CaCO₃).

Malgré l'intérêt croissant de la communauté scientifique face à la progression et aux effets de l'acidification dans l'Arctique Canadien, peu d'études récentes dressent un portrait complet du système des carbonates, qui régit le sort du CO₂ dans l'eau de mer, dans cette région. Un vaste jeu de données composé d'observations recueillies entre 2003 et 2016 est utilisé dans le but de caractériser et de suivre l'évolution temporelle de ce système dans l'Archipel Arctique Canadien, le Basin Canadien et la Baie de Baffin. Les résultats indiquent que la quasi-totalité des eaux de surface de cette région sont un puits de CO₂ (absorbent le CO₂ atmosphérique) durant l'été et que celles du Basin Canadien et du Golfe de la Reine-Maud sont sous-saturées par rapport à l'aragonite. Des séries temporelles permettent de quantifier la forte variabilité du système des carbonates dans cette région dynamique, où l'activité biologique est responsable d'environ 30% de la variabilité du CID (carbone inorganique dissout) en surface. Par conséquent, l'observation directe du signal d'acidification requerra des séries temporelles plus longues, de l'ordre de 20 à 30 ans dans le cas du pH, de la pCO₂ et de Ω_A .

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Author Contributions

The results of this thesis research are presented in manuscript form in Chapter 2. The first chapter, a general introduction, provides a brief overview of the causes and known effects of ocean acidification, a physical description of the study area and the objectives of this study. The co-authors of the manuscript are (in order) Alfonso Mucci (McGill University) and Helmuth Thomas (Dalhousie University). The contributions of these authors are as follows: AM and HT provided data and guidance through informal discussions; AM reviewed and edited the manuscript.

Alfonso Mucci supervised the making of this thesis. The principal author contributed the remainder of the thesis, including the figures, data compilation, processing, analysis and interpretations. Overlaps in text between the general introduction and the manuscript abstract, introduction and conclusions were minimized, but remain inevitable.

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Chapter 1: General Introduction

1.1 Background - Ocean Acidification

1.1.1 The Anthropogenic CO₂ Source

Ocean acidification resulting from the massive release of anthropogenic carbon dioxide (CO₂) to the atmosphere is changing seawater biogeochemistry in ways and extents that have yet to be fully understood. The global atmospheric CO₂ concentration has increased by over 40% from the 1750 pre-industrial level of ~280 ppm (MacFarling Meure et al., 2006), at a rate previously unseen in geological history, and recently exceeded the symbolic threshold of 400 ppm (NOAA/ESRL; Dlugokencky and Tans, 2018). Between 2002 and 2011, the mean decadal rate of atmospheric CO_2 concentration increase was the highest ever observed directly, at 2.2 ppm yr⁻¹ (Ciais et al. 2013). This recent exponential growth in CO₂ emissions makes the study of recent changes in atmospheric and seawater chemistry particularly critical. Fossil fuel extraction and combustion account for the vast majority of the anthropogenic CO₂ emissions, followed by changes in land use, such as deforestation aimed at the creation of agricultural lands (Ciais et al., 2013; Le Quéré et al., 2018). The measured atmospheric CO₂ concentration only accounts for a fraction of the atmospheric emissions as a large portion of these is removed from the atmosphere by various natural processes operating on different timescales. These include photosynthesis (land sink) on short timescales (1- 10^2 years), exchanges with the surface ocean and the deep-ocean reservoir through the biological and the solubility pumps on timescales of $10-10^3$ years, as well as silicate weathering on geological timescales (10^4 - 10^6 years).

1.1.2 Air-Sea Gas Exchange

CO₂ is constantly being exchanged between the oceanic and atmospheric reservoirs, along with other gases. The flux of CO₂ across the air-sea interface varies spatially and temporally in the global oceans and can be described and modelled with two main parameters: the gas transfer velocity (k) and the air-sea pCO₂ gradient (Δ pCO₂), respectively influenced by kinetic (wind speed, sea-surface roughness, etc.) and thermodynamic (temperature, biological effects, etc.) forcing. Equation 1 (Wanninkhof, 2009) illustrates this basic relationship:

(1)
$$F = k(C_w - C_o)$$

where *F* is the flux of a non-reactive gas and C_w and C_o are the concentrations of this gas at the water surface (in equilibrium with the lower atmosphere) and in the mixed layer below, respectively. This equation is derived from the commonly used stagnant film model, which characterizes the rate of gas exchange as limited by the rate of molecular diffusion across a thin, quiescent layer of water of fixed thickness (Liss and Slater, 1974). Various studies have estimated the global oceanic yearly net carbon dioxide uptake, with invariably large uncertainties. Takahashi et al. (2009) used surface ocean pCO₂ measurements to estimate a yearly carbon flux into the ocean of 2±1 PgC for a 2000 reference year, and a mean global surface pCO₂ increase of 1.5 µatm yr⁻¹. Le Quéré et al. (2018) used a carbon-budget approach to estimate the same flux to 2.1±0.5 PgC yr⁻¹ in the 2000-2010 decade, increasing to 2.6±0.5 PgC yr⁻¹ in 2016. Other studies corroborate this increase in the ocean carbon uptake (e.g. Majkut et al., 2014). Bates and Mathis (2009) compiled published values of the Arctic Ocean's contribution to the global oceanic CO₂ uptake, which range from 81 to 199 TgC yr⁻¹, or 5% to 14% of the global oceanic uptake. More recent estimates sit at the upper end of this range (166±60 TgC yr⁻¹, MacGilchrist et al., 2014; 180±130 TgC yr⁻¹, Yasunaka et al., 2018).

1.1.3 The Carbonate System

The world ocean absorbed roughly a third of the anthropogenic CO₂ released to the atmosphere since the industrial revolution (Sabine et al., 2004). Changes in seawater chemistry resulting from this addition of dissolved inorganic carbon (DIC, defined as the sum of the concentrations of all inorganic carbon species or $[H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$, where $[H_2CO_3^*] = [CO_{2(aq)}] + [H_2CO_3]$ to the surface ocean are governed by the chemistry of the carbonate system and can be described by the following set of reactions.

$$H_2O + CO_{2(aq)} \leftrightarrow H_2CO_3$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$

After CO₂ goes into solution (equation 2), it reacts with water to form carbonic acid (equation 3), which, in the typical pH range of surface oceans, dissociates into bicarbonate (HCO₃⁻) and hydrogen (H⁺) ions. The proton released through this reaction (equation 4) increases the concentration and activity of H⁺, decreasing the pH of the solution. Subsequently, carbonate ions (CO₃²⁻) present in solution will neutralize a portion of the free hydrogen ions through the formation of bicarbonate ions (equation 5). The resultant decrease in carbonate ion concentration affects the capacity of calcifying organism to precipitate their shells or exoskeletons and the preservation of carbonate minerals (CaCO₃) in marine sediments, by decreasing the saturation state of seawater with respect to these minerals. The saturation state is defined as:

(6)
$$\Omega = \frac{(Ca^{2+})(CO_3^{2-})}{K_{sp}^0} = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}^8}$$

where (i) are activities and [i] are concentrations. K^{o}_{sp} is the thermodynamic solubility product and K^{*}_{sp} is the stoichiometric solubility product of the calcium carbonate mineral of interest (e.g. Plummer and Busenberg, 1982; Mucci et al., 1983). Their thermodynamic values vary with temperature and pressure whereas the latter is also a function of the solution composition (salinity).

Calcite and aragonite are the two most common CaCO₃ polymorphs (respectively orthorhombic and hexagonal) precipitated inorganically or biologically from seawater, although most of the CaCO₃ that accumulates in ocean sediments is biogenic and made up of the structures (tests, shells, exoskeletons) of various marine organisms. The precipitation of inorganic calcium carbonate minerals is dependent on the saturation state of the parental solution, such that, excluding biological effects, supersaturated waters $(\Omega > 1)$ favor carbonate precipitation and undersaturated waters $(\Omega < 1)$ favor dissolution. The saturation state of seawater with respect to aragonite is commonly used as a proxy for ocean acidification, as the mineral is 50% more soluble than calcite (Mucci, 1983) and is therefore more sensitive to changes in seawater pH. The inorganic precipitation of aragonite from seawater is favored over calcite by the presence of sulfate (SO42-) and magnesium (Mg²⁺) in seawater, both of which inhibit calcite nucleation and growth by adsorption and destabilization of the mineral surface and lattice (Bischoff et al., 1987; Dove and Hochella, 1993; Davis et al., 2000; Sun et al., 2015). Higher saturations states, Mg²⁺:Ca²⁺ ratios, pressures and temperatures also favor aragonite precipitation (Burton and Walter, 1987; Morse et al., 1997; Sun et al., 2015), but organisms have developed a number of mechanisms to precipitate CaCO₃ of various mineralogies (e.g. Mackenzie and Andersson, 2013; Erez, 2003).

The surface ocean, where most biological activity occurs, is typically oversaturated with respect to aragonite. As the aragonite solubility (K^*_{sp}) increases with depth in response to increasing pressure and decreasing temperature, the saturation state of seawater with respect to aragonite also decreases with depth in the oceanic water

column. It is further reduced by a lowering of pH as CO₂ resulting from the microbiallymediated remineralization of settling organic matter is added to the solution. Below the depth of aragonite saturation ($\Omega_A = 1$), practically no aragonite accumulates in sediments. This sediment marker horizon is referred to as the aragonite compensation depth (ACD). The ACD is generally much shallower than the calcite compensation depth (CCD), which has the same formal definition applied to calcite but generally occurs well below the calcite saturation depth (Ω_C =1). As ocean acidification proceeds and carbonate ion concentrations decrease throughout the water column, the ACD and CCD are becoming shallower (e.g. Sulpis et al., 2018).

Total alkalinity or Titration alkalinity (TA) is another critical parameter of the carbonate system. It is a measure of the neutralizing capacity of a solution upon the addition of an acid and is defined by (Dickson, 1981):

$$TA = [HCO_3^-] + 2[CO_3^-] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-]$$

+ [HS^-] + [NH_3] + 2[S^{2-}] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4]

where $[HCO_{3^2}] + 2[CO_{3^2}] + [B(OH)_{4^2}]$ accounts for most of the seawater TA in the surface ocean, as the concentration of other species are negligible. The buffer capacity of seawater is related to TA and describes the ability of a solution to resists changes in pH upon the addition of an acid or a base. It greatly increases if the solution is in contact and can exchange CO₂ with a gas phase such as the atmosphere. TA is a nearly conservative (proportionally to salinity) property in the open ocean, as it is affected only by CaCO₃ dissolution/precipitation and slightly by biological activity (photosynthesis/respiration; Zeebe and Wolf-Gladrow, 2001). The ratio of DIC:TA is expected to increase with the progression of ocean acidification, resulting in a decrease in the seawater buffer capacity or its ability to absorb CO₂. This will also translate in an increase of the Revelle factor, defined as the change of pCO₂ resulting from a given change in DIC (Revelle and Suess, 1957).

1.1.4 Ocean Acidification and Marine Organisms

Ocean Acidification would not be a subject of great scientific interest without its potentially devastating effects on marine ecosystems. Any disruption to the biochemical balance of the oceans will undoubtedly affect species of all trophic levels. The impact of acidification on primary producers is of particular importance, as any change at this level will rapidly propagate up the food chain.

Marine calcifying organisms secrete CaCO₃ 'hard parts' (tests, shells, exoskeletons). These include primary producers such as coccolithophores (phytoplankton - calcitic), foraminifera (zooplankton - calcitic), pteropods (zooplankton - aragonitic), as well as a diverse range of larger organisms such as corals, molluscs, echinoderms and some crustaceans. Their growth (calcification) rate and ability to photosynthesize are largely dependent on the chemistry of their living environment.

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Whereas the inorganic precipitation of carbonate minerals is straightforwardly correlated to the carbonate saturation state of the seawater (Zhong and Mucci, 1989), relating the calcification rate of marine organisms to external parameters such as Ω and pH requires more scrutiny. Meta-analyses investigating these relationships indicate a wide variety of species-specific responses, most indicating a decrease in calcification rates and deleterious metabolic responses (photosynthesis, survival, etc.) under increased pCO₂, lowered Ω and pH conditions, although some species show negligible or positive responses (Kroeker et al., 2013; Doney et al., 2009). More recently, following a detailed study of coccolithophore response to OA, Meyer and Riebesell (2015) reported that despite important intra- and inter-species variability, the overall response of coccolithophores to acidification was one of hindered growth. It is important to note that these results are limited in their scope and applicability to natural systems by the isolated nature and the generally short duration of the experiments from which they stem, which largely do not account for interactions between different species or long-term adaptive mechanisms. Nonetheless, these findings suggest that as acidification proceeds, species more resistant to high-CO₂ conditions will replace those that are more widespread today, with unknown consequences on the marine trophic structure as a whole.

The mechanisms responsible for the varied biological responses to acidified conditions are also poorly understood. A depletion of CO₃²⁻ ion concentrations (and saturation state) in seawater constitutes the simplest explanation for diminished biogenic CaCO₃ production, but the existence of organisms exhibiting unchanged or increased calcification rates under lowered carbonate ion concentrations (higher pCO₂) suggests

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calcification is at least partly independent of the surrounding water saturation state for these organisms (Findlay et al., 2009). Many 'vital effects' and intricate chemical and biological processes need to be further investigated, such as the ability of organisms to maintain pH homeostasis in high-CO₂ conditions (Cyronak et al., 2015). The consequences of ocean acidification must also be considered along with other climatechange related processes like warming and eutrophication as well as changes in ocean oxygenation and circulation.

1.2 Study Area: The Canadian Arctic

The area investigated in this study, referred to as the Canadian Arctic, is centered around the Canadian Arctic Archipelago (CAA), a chain of islands cut by narrow channels on the northern edge of the North American continental shelf. It includes two deep basins adjacent to the archipelago: to the west, the Canada Basin and to the east, Baffin Bay, enclosed between Baffin Island and Greenland. The overarching circulation pattern in this region is the flow of surface water from the North Pacific to the North Atlantic, counterbalancing the higher sea-level of the North Pacific due to the higher precipitation and lower evaporation rates in this ocean (Stigebrandt, 1984). Approximately 35% of the surface water transported out of the Arctic Ocean annually does so through the CAA and Baffin Bay, the remainder via Fram Strait (Serreze et al., 2006). The dominant surface circulation features are depicted in figure 2.1.

1.2.1 Canada Basin

The 3500 m-deep Canada Basin makes up the southern portion of the larger Amerasian Basin, which forms the central Arctic Ocean along with the Eurasian Basin. The 1500-m deep Lomonosov Ridge separates the Amerasian and Eurasian Basins, effectively isolating the deep waters of the Canada Basin, upwards of 1000 years in age, from the global oceanic circulation (MacDonald and Carmack, 1991). Most of the Canada Basin data used in this study were collected in the Beaufort Sea, located in the southwest corner of the basin, and bordered by the North American shelf to the south and the CAA to the east.

The mean circulation in the Beaufort Sea is defined at the surface by the clockwise (anticyclonic) Beaufort Gyre. At depth, this feature reverses to form the counter-clockwise (cyclonic) Beaufort undercurrent (Carmack and McDonald, 2002). The Beaufort Gyre is described as the largest freshwater reservoir of the Arctic Ocean, meaning that its surface waters have a relatively low salinity ($S_P \sim 25$ -30) that translates to a high 'freshwater equivalent' of ~15-20 m (Proshutinsky et al., 2009). The accumulation of low-salinity water is maintained through Ekman Pumping, a process by which a cyclonic wind pattern drives convergence and downwelling of surface waters. Apart from sea-ice melt (see 1.2.2), the Mackenzie River is the largest source of freshwater in the Beaufort Sea. Owing to climate change, its discharge has been increasing by ~1.5% per decade since the mid-20th century (Rood et al., 2017).

The water-mass structure in the Beaufort Sea and along the Mackenzie Shelf has been described by several authors (e.g., Carmack et al., 1989, MacDonald et al., 1989, Lansard et al., 2012). Although the nomenclature varies, they agree on the presence of a low-salinity (S_P <33) surface layer consisting of Pacific waters entering the Arctic Ocean through the Bering Strait and affected by seasonally-variable inputs of sea-ice melt and meteoric water. The upper ~50 m of this layer is named Polar Mixed Layer and displays uniform properties during the winter. Below, we find an intermediate (dominant below ~200 m to ~1600 m) layer of Atlantic waters, that entered the Arctic Ocean through Fram Strait and the Barents Sea and circulated through the Eurasian and Amerasian Basins (34.4<S<34.9). Finally, the water column structure is completed by a layer of bottom waters with 34.88<S_P<34.96. Pacific waters found in the halocline (50-200 m) are typically divided into summer and winter varieties, the latter being referred to as the Upper Halocline Water or Layer (UHW or UHL) and characterized by a temperature minimum at S_P~33.1, high pCO₂ and high nutrient concentrations. Atlantic waters are also separated into the Fram Strait Branch (temperature maxima at ~450 m or S_P=34.8) and the Barents Sea Branch (S_P=34.88 at ~900 m), the former dominating the Atlantic component in the Canadian Basin (McLaughlin et al., 2004).

1.2.2 Canadian Arctic Archipelago

Shallow pathways through the CAA make up the major routes for the flow of surface waters from the Beaufort Sea to Baffin Bay and ultimately the North Atlantic Ocean. Water enters the CAA from the Canadian Basin via the Amundsen Gulf, M'Clure Strait and between M'Clure Strait and Ellesmere Island through the Queen Elizabeth Islands. Some water also enters the CAA from the central Arctic Ocean through Nares Strait, and from the Atlantic through Baffin Bay (McLaughlin et al., 2004). The circulation in this area is complex, as the width of many channels throughout the CAA allows for opposing flows and localized circulation features, seasonally affected by the presence of sea-ice (Leblond, 1980). Bathymetry also exerts a strong control over circulation and water mass structures in the CAA. The shallow sill depths that surround it (250-500 m) restrict the inflow of water to the upper layers of the Beaufort Sea and Baffin Bay, so that mostly fresher water of Pacific origin and the upper portion of the Atlantic intermediate layer flow over the continental shelf. The upward movement of water masses (visible by a rising of the isopycnals at the Beaufort Sea-CAA boundary) as they encounter the continental shelf at the 375-m deep M'Clure Strait forces mixing between Pacific and Atlantic waters, the latter being found only below depths of 135 m in the CAA. The temperature minimum characteristic of Pacific waters in M'Clure Strait tends to disappear eastward due to this mixing (McLaughlin et al., 2004).

Surface waters also become colder and more saline due to ice formation as they move through the CAA towards Baffin Bay during the winter (Prinsenberg and Bennett, 1987). The eastward progression of the Canada Basin Atlantic layer is effectively halted by the shallow 125-m sill at Barrow Strait, so that only surface and Pacific waters make it through to Lancaster Sound (Bidleman et al., 2007). As a result, whereas the water mass structure west of Barrow Strait is similar to that of the Canada Basin, the water masses east of the sill are similar to those found in Baffin Bay.

1.2.3 Baffin Bay

Baffin Bay is a semi-enclosed basin lodged between Baffin Island to the west and Greenland to the east. It connects with the Arctic Ocean via the Canadian Arctic Archipelago through Lancaster Sound and Jones Sound (500 and 190 m sill depths, respectively) and directly through Nares Strait (220m sill depth), as well as with the Labrador Sea and North Atlantic Ocean through the 640-m deep Davis Strait. The maximum water depth in Baffin Bay exceeds 2300 m. Northwestern Baffin Bay hosts polynyas in Jones and Lancaster Sounds, which join in spring to form the North Water Polynya, one of the largest polynyas in the Northern Hemisphere (Lewis et al., 1996). Muench (1971) recognized the Atlantic and Arctic Oceans as the two major sources of Baffin Bay waters, although, as pointed out by Jones et al. (1998, 2003), Pacific waters make up most of the Arctic input into Baffin Bay. The large-scale circulation within Baffin Bay is cyclonic, with the northward West Greenland Current (WGC) entering through the

eastern side of Davis Strait, bifurcating to the west near Cape York and joining the southward Baffin Island Current (BIC), which exits Baffin Bay through the western Davis Strait (Tang et al., 2004).

The West Greenland Current (WGC) brings warm and saline Atlantic water from the Labrador Sea northward, along the 500-m isobath of the Greenland Shelf slope (Bourke et al., 1989). It is recognized by a temperature maximum at salinities above 33.9 (Münchow et al., 2015). Upon entering Baffin Bay at the bottom of the eastern Davis Strait, Atlantic water has a potential temperature and salinity of $\theta \sim 4$ °C and S_P~34.78 (Cuny et al., 2005). It is substantially modified within Baffin Bay as it cools and mixes with Arctic water near the North Water Polynya (Melling et al., 2001). The WGC bifurcates towards the west, following bathymetry, near the latitude of Lancaster Sound and joins the Baffin Island Current.

The southward Baffin Island Current (BIC) results from inputs of Arctic waters from Smith Sound (Nares Strait), Jones Sound and Lancaster Sound, with a significant proportion of modified WGC water (Münchow et al., 2015). Jones et al. (2003) estimated, based on phosphate-nitrate ratios, that Arctic water entering Baffin Bay through Jones Sound and Lancaster Sound was entirely of Pacific provenance, while the flow from Nares Strait into Smith Sound contained mostly Pacific-origin water near the surface and Atlantic-origin water below 150 m or at S_P>33.3, both from the southern Canada Basin. Fissel et al. (1982) documented the intrusion of the BIC into eastern Lancaster Sound, through which it travels westward, generally for 50-100 km on the north side before crossing over to the south side and reversing direction. Further south, the BIC stays within 100 km of the Baffin Island coast, transporting waters characterized by a constant temperature (-1.6°C) from the surface to S_P=33.7 and a temperature maximum of + 1°C at S_P = 34.5 (Munchow et al. 2015) before exiting Baffin Bay on the western side of Davis Strait.

Tang et al. (2004) also described the general structure of the Baffin Bay water column into three layers: 1) A layer of cold and low-salinity Arctic water originating from the northwestern Jones, Smith and Lancaster Sounds and Arctic water that circles Greenland and enters through the eastern Davis Strait. This last layer is characterized by sub-zero temperatures, extends down to the temperature minimum at S_P=33.7, and is deeper (300 m) in the west than in the east (100 m). 2) A warm Atlantic mid-layer from 300 to 800 m depth with T > 0°C and S_P > 34 is carried by the WGC northward and the BIC southward and 3) A deep layer from 1200 m to the bottom, with near-constant salinities of 34.5, for which the formation mechanisms are still debated but are confined within Baffin Bay, as the sill depths prevent circulation of dense waters from other basins. The surface layer in Baffin Bay is more saline (S_P= 33.7) than the Arctic inflows into the area. Thus, it must be influenced by considerable brine rejection during ice formation (Rudels, 2011).

1.2.4 Ocean Acidification in the Canadian Arctic

The Arctic Ocean is particularly vulnerable to acidification for a number of reasons. First, its low alkalinity and carbonate ion concentrations translate into a poor buffer capacity relative to other oceans, including the Southern Ocean (Shadwick et al., 2013). The buffer capacity decreases further in cold water, owing to the temperature dependency of the carbonic acid and bicarbonate dissociation constants. Second, the rapid melting of the ice cover (Tivy et al., 2011) promotes CO_2 uptake by the ocean in two ways: 1) through a direct exposure, upon ice melting, of the ocean surface to the atmosphere and uninhibited gas exchange across the air-sea interface and 2) through the dilution of surface DIC and TA by sea-ice melt waters (Rysgaard et al., 2009; Bates et al., 2014). Warming and increased stratification due to a freshening of the surface may eventually counteract these processes by elevating surface pCO₂ and inhibiting the export of CO₂ to deeper waters (Cai et al., 2010; Else et al., 2013). Brine rejection during increased firstyear ice formation in the winter might also enhance gas exchange by exporting carbon below the surface mixed layer (Rysgaard et al., 2011), although some observations suggest that brines of relatively low density or small volume stay at the water-ice interface until the onset of spring melting, inhibiting surface water CO₂ uptake (Miller et al., 2011; Fransson et al., 2013). Additionally, wind-driven upwelling of metabolic CO₂-rich water of Pacific origin near the shelves of the Beaufort Sea (Mucci et al., 2010; Mol et al., 2018) and advection of pre-acidified Atlantic water throughout the study area (Luo et al., 2016) exacerbate the vulnerability of the region to acidification.

Observations carried out in the summer months indicate that, excluding certain areas of upwelling, surface waters of the Beaufort Sea (Mucci et al., 2010), CAA and Baffin Bay (Burgers et al., 2017; Geilfus et al., 2018) are undersaturated with respect to atmospheric CO₂ and thus act as a net CO₂ sink.

The shoaling of aragonite-undersaturated waters (or the aragonite saturation depth; $\Omega_A \leq 1$) at the surface, an important threshold in most acidification studies, has been documented relatively recently in the Canada Basin and the CAA. The upper 2000 meters of the Canada Basin water column were invariably supersaturated with respect to aragonite (Ω_A =1.1-1.5) in 1997 (Jutterström and Anderson, 2004). A rescued historical dataset dating back to 1974 identifies the first occurrence of aragonite undersaturation in the upper halocline (100-200m) of the same area near the year 2000, and surface undersaturation in the following decade (Miller et al., 2014). Multiple studies corroborate this progressive acidification of Arctic Ocean waters, with aragonite-undersaturated (Ω_A < 1) surface waters first appearing on freshwater-dominated shelves (Chierici and Fransson, 2009; Bates et al., 2009; Azetsu-Scott et al., 2010). By 2008-2010, aragoniteundersaturated surface waters were ubiquitous throughout the southern Canada Basin, the Beaufort Sea and were found in the western CAA (Robbins et al., 2013, Qi et al., 2017; Yamamoto-Kawai et al., 2013). This rapid decrease in Ω_A results mostly from the increase in sea-ice melt in the region (Yamamoto-Kawai et al., 2009; 2011). Saturation states with respect to aragonite remain above saturation but relatively low (Ω_A =1.5-2.5) in the eastern CAA and Baffin Bay (Azetsu-Scott et al., 2010).

1.3 Objectives

Since no data were collected for this study specifically, the objectives of this work were designed according to the available dataset, which consists of 420 stations visited during seven oceanographic research cruises carried out between 2003 and 2016. Although the Canada Basin and Baffin Bay are an integral part of this study, the Canadian Arctic Archipelago and the Beaufort Sea will be more heavily represented, as most of the stations are located in these areas.

Very little research focusing on the carbonate system of the Canadian Arctic after 2010 has been published in the last decade, and recent time series of ocean acidification are inexistent for this region. Accordingly, the objectives of this study are to 1) describe the recent state of the carbonate system in the region with observations made from 2014 to 2016, 2) assess the suitability of our dataset to the construction of time series, and, if possible, identify any temporal trends in the carbonate system, related or not to ocean acidification and 3) quantify the interannual variability in the carbonate system of the region, its different contributing processes, and estimate the temporal scale at which the ocean acidification signal is likely to emerge from this interannual variability.

2. The State and Variability of the Carbonate System of the Canadian Arctic in the Context of Ocean Acidification: 2003-2016

Contributing co-authors: Alfonso Mucci and Helmuth Thomas

Abstract

Ocean acidification driven by the uptake of anthropogenic CO₂ by the surface oceans constitutes a potential threat to the health of marine ecosystems around the globe. The Arctic Ocean is particularly vulnerable to acidification due to its relatively low buffering capacity and, thus, is an ideal region to study the progression and the effects of acidification before they become globally widespread. The appearance of undersaturated surface waters with respect to the carbonate mineral aragonite ($\Omega_A < 1$), an important threshold beyond which the calcification and growth of some marine organisms might be hindered, has recently been documented in the Canada Basin and adjacent Canadian Arctic Archipelago. Nonetheless, few of these observations were made in the last five years and the spatial coverage in the latter region is poor. Additionally, the strong variability inherent to this extremely dynamic shelf environment renders the temporal imprint of ocean acidification on carbonate system parameters (pH, pCO₂, DIC, Ω) virtually indistinguishable on decadal timescales. We use a dataset of carbonate system parameters measured in Canadian Arctic Archipelago and its adjacent basins to describe the recent state of these parameters across the Canadian Arctic and investigate the amplitude and sources of the system's variability. Our findings reveal that, in addition to

the surface of the Canada Basin, the entire water column of the Queen Maud Gulf was undersaturated with respect to aragonite in 2015 and 2016. We estimate that approximately a third of the interannual variation in surface DIC in the CAA results from fluctuations in biological activity, and use the concept of time of emergence (ToE) to constrain the length of time series needed to directly observe the ocean acidification signal in the Canadian Arctic to between 20 and 30 years for pH, pCO₂ and Ω_A and upwards of 100 years for DIC.

2.1 Introduction

Ocean acidification and its repercussions on marine ecosystems constitute an important consequence of the ongoing rise in atmospheric carbon dioxide (CO₂) concentrations. The world's oceans absorbed approximately a third of the anthropogenic CO₂ released to the atmosphere over the last two centuries of industrial activity (Sabine et al., 2004) and are currently a sink for ~24% of global annual anthropogenic carbon emissions (Le Quéré et al., 2018). This consistent carbon uptake by the surface oceans has well defined impacts on seawater chemistry, including a decrease of pH resulting from the release of hydrogen ions (H⁺) following the dissociation of carbonic acid (H₂CO₃), the product of the reaction between water and dissolved CO₂. A large fraction of the hydrogen ions released by this reaction is neutralized by carbonate ions (CO₃²⁻), leading to a decrease of their concentration and, concomitantly, the saturation state of seawater

with respect to the carbonate minerals calcite and aragonite (CaCO₃ polymorphs). The saturation state is defined by:

(1) Ω_{C,A}= [Ca²⁺][CO₃²⁻] / K^{*}_{SP}

where square brackets denote concentrations and K^*_{SP} is the stoichiometric solubility product of calcite or aragonite at a given temperature, pressure and salinity.

The combination of these phenomena is most often referred to as ocean acidification (OA). As it proceeds, the dissolved inorganic carbon concentration (DIC; the sum of $[H_2CO_3^*]$, $[HCO_3^-]$ and $[CO_3^{2-}]$) in the surface ocean is expected to increase relative to the total alkalinity (TA; the capacity of a solution to neutralize protons), as the latter is nearly conservative in the surface ocean (Wolf-Gladrow et al., 2007). The global mean surface ocean pH currently sits ~0.1 units below its preindustrial value (Orr et al., 2005) and, according to Earth system models under the IPCC's "business as usual" RCP8.5 emission scenario, is predicted to decrease by an additional 0.3 units by the end of this century (Bopp et al., 2013).

Marine calcifying organisms, many of which are important primary producers (e.g., coccolithophores), extract the constituents of their calcitic or aragonitic tests (shells) from seawater. Their ability to do so is directly dependent on the saturation state of the surrounding water. Supersaturated seawater ($\Omega > 1$) will favor carbonate precipitation whereas undersaturated seawater ($\Omega < 1$) favors carbonate dissolution. The majority of calcifying organisms, such as planktonic foraminifera and coccolithophores, undergo

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dissolution or exhibit substantially hindered growth when exposed to undersaturated seawater (e.g. Mostofa et al., 2016). Calcifying organisms found in the Arctic Ocean are subject to rapid environmental changes, as this polar ocean is warming more rapidly than others (Serreze et al., 2011) and is particularly vulnerable to acidification due to the low alkalinity and correspondingly weak buffer capacity of its cold waters (Shadwick et al., 2013). The CO₂ uptake by Arctic surface waters is further promoted by the rapidly melting seasonal ice cover (e.g. Stroeve et al., 2012), which exposes a gradually larger area of the ocean to gas exchange with the atmosphere and whose melt-water dilutes calcium concentrations, alkalinity and carbonate ion concentrations, further decreasing Ω .

The Canadian Arctic Archipelago (CAA) and its adjacent deep basins, the Canada Basin (CB) and Baffin Bay (BB, figure 2.1), are part of the region projected to undergo the largest reduction in ice cover and consequently the largest decrease in surface pH (~0.6) and Ω (1 and 0.7 for $\Omega_{\rm C}$ and $\Omega_{\rm A}$, respectively) over the 21st century (Popova et al., 2014). Recent observations (e.g. Yamamoto-Kawai et al., 2009b; Robbins et al., 2013; Qi et al., 2017) hint at a significant decrease of the aragonite saturation state of surface waters as well as a rapid expansion of the undersaturated area in the Canada Basin, but most of these time series predate 2010 and do not extend geographically to the CAA and Baffin Bay.

In this study, we use a large observational dataset for this part of the Arctic to 1) describe the recent state of the carbonate system and its spatial variability in the

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Canadian Arctic Archipelago and its adjacent basins, 2) investigate the interannual variability in carbonate system parameters and identify any visible temporal trends using time series spanning from 2003 to 2016 and 3) estimate the length of time series needed to observe the ocean acidification signal, despite the high variability in this region.

2.2 Study Area

2.2.1 Canada Basin

The Canada Basin (CB), Canadian Arctic Archipelago and Baffin Bay accommodate the flow of surface waters from the North Pacific to the North Atlantic (Stigebrandt, 1984), as well as circulation of Atlantic waters at greater depths. The water mass structure of the southern Canada Basin is representative of these broad circulation patterns and can be summarized as follows (Carmack et al., 1989; MacDonald et al., 1989; Lansard et al., 2012): a relatively cold and fresh surface layer that contains significant fractions of meteoric water (river discharge and precipitation) and sea-ice melt in the summer and becomes homogeneous in winter; an intermediate layer (~50-200m) of advected Pacific waters, often divided into summer and winter varieties, the latter being distinctively rich in nutrients and metabolic CO_2 and recognizable by a temperature minimum in the upper halocline; a layer of warm (~0.5°C) and saline (S_P>34) Atlantic water; a cold bottom layer with practical salinities (S_P) reaching 34.85. The main surface

circulation feature in this area, the clockwise Beaufort Gyre, is the largest freshwater reservoir in the northern oceans, formed through Ekman pumping (Proshutinsky et al., 2009). This feature is reversed at depth. The main source of freshwater to the Beaufort Sea (the southwest portion of the Canada Basin) is the Mackenzie River (Carmack and MacDonald, 2002), although the contribution of sea-ice melt is significantly increasing along with the accelerating reduction in ice cover (Yamamoto-Kawai et al., 2009a). The supply of freshwater at the surface, combined with the advection of pre-acidified waters from the Pacific (100-200 m) and the Atlantic (below 400 m; Luo et al., 2016) result in the presence of three distinct and expanding undersaturation horizons in the Canada Basin (Wynn et al., 2016).

2.2.2 Canadian Arctic Archipelago

The CAA is a series of islands on the Canadian continental shelf, through which complex circulation patterns unfold in narrow and relatively shallow channels (<500 m). See McLaughlin et al. (2004) for a detailed description of the circulation and water mass processes in this area. The prominent pathway for the eastward flow of Canada Basin water masses into Baffin Bay extends along the 74th parallel from M'Clure Strait to Lancaster Sound. A shallow 125-m sill at Barrow Strait, located centrally in the archipelago, inhibits the eastward flow of Atlantic waters, so that only surface and Pacific-origin waters reach Baffin Bay (Bidleman et al., 2007). The properties of these water masses are substantially modified during this transit (McLaughlin et al., 2004). East of
Barrow Strait, Atlantic waters originating from the Labrador Sea penetrate the archipelago through Baffin Bay. Smaller inflows of water from the deep Arctic Ocean into the archipelago occur through the Queen Elizabeth Islands (North-East) and Nares Strait; minor outflows occur through Jones Sound and into Hudson Bay via Foxe Basin. Apart from the Mackenzie River, whose discharge is limited to the Beaufort Sea and Amundsen Gulf, the southern portion of the CAA receives a considerable amount of freshwater from other large North American rivers (Coppermine, Burnside, Black).

2.2.3 Baffin Bay

The oceanographic regime of Baffin Bay is distinct from that of the CAA and CB, as it receives multiple inputs from both the Arctic and Atlantic Oceans. Cold and relatively fresh Arctic and Pacific-derived waters enter this 2300-m deep semi-enclosed basin through the Nares Strait as well as Jones and Lancaster Sounds (Muench, 1971; Jones et al., 1998, 2003). Warmer and more saline Atlantic Ocean waters are transported from the Labrador Sea by the West Greenland Current (WGC) into Baffin Bay through the eastern side of Davis Strait, circulate cyclonically, i.e., in an anti-clockwise direction, before joining the southward Baffin Island Current (BIC) which exits Baffin Bay through the western Davis Strait (Bourke et al., 1989, Munchow et al., 2015). Atlantic Ocean waters are modified as they mix with Arctic inflows in Northern Baffin Bay, near the North Water Polynya (Melling et al., 2001). The resulting water mass structure is described by Tang et al. (2004) as: 1) a cold (T<0°C) and relatively fresh (S_P<33.7) surface layer

representing the mixed Arctic inputs, 2) a warm (T>0°C) and saline (S_P>34) Atlantic Ocean water layer found at depths of ~300 to 800 m, and 3) a deep layer of nearly constant salinity (S_P = 34.5).

2.3 Methods

The dataset used in this study comprises data from 420 stations visited during various research cruises carried out aboard the CCGS Amundsen between 2003 and 2016. Table 1 summarizes the timeframe and relevant data acquired during each cruise; figure 1 shows the position of each sampling station. Although ice conditions restricted most observations to the summer months, two winter time-series, acquired in 2003-2004 (CASES, Miller et al., 2011) and 2007-2008 (CFL, Shadwick et al., 2011) are included in the dataset.

2.3.1 Sampling and measurements

Seawater was sampled separately for each measured parameter from Niskin bottles attached to a Rosette system equipped with a Seabird SBE 911plus Conductivity-Temperature-Depth (CTD) sensor, which collected *in-situ* practical salinity (S_P) and temperature data throughout the water column. The conductivity/salinity probe was calibrated post-cruise against measurements carried out on discrete seawater samples

using a Guildline Autosal 8400 salinometer (accuracy of \pm 0.002 or less), itself calibrated with IAPSO standard seawater. Samples used for pH determination were drawn directly from the Niskin bottles into 125 mL low density polyethylene (LDPE) bottles with no headspace to avoid gas exchange with surrounding air and left to thermally equilibrate in a temperature bath set to 25.0 (\pm 0.1) °C. pH, on the total proton scale (pH_T), was then measured spectrophometrically on a Hewlett-Packard 8453 UV-visible diode array spectrophotometer using m-Cresol purple (Clayton and Byrne, 1993) and Phenol red (Robert-Baldo et al., 1985) indicators at 434 and 578 nm or 433 and 558 nm, respectively, in a 5-cm guartz cell. Daily calibrations were performed with TRIS buffer solutions at practical salinities of 25 and/or 35, depending on the salinity range of the samples. The reproducibility was found to be ±0.005 pH units or better, based on duplicate measurements made on the same samples with the same or both indicators. Samples destined for total alkalinity (TA) and dissolved inorganic carbon (DIC) analyses were drawn directly from the Niskin bottles into 250 or 500 mL glass bottles with ground-glass stoppers, poisoned with mercuric chloride (HgCl₂) to halt biological activity, and sealed with Apiezon M grease.

TA and DIC from the GEOTRACES 2009 and all post-2010 cruises were measured onboard or at Dalhousie University on a Marianda VINDTA 3C instrument, following the protocol described by Dickson et al. (2007) and calibrated with Certified Reference Materials (CRM) provided by A.G. Dickson (Scripps Institute of Oceanography). The precision of the instrument was found to be \pm 2-3 µmol/kg based on repeated CRM analyses. The remaining DIC and TA analyses were performed respectively on a SOMMA

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instrument (Johnson et al., 1993) fitted to a UIC 5011 coulometer and by potentiometric titration using a Radiometer Titrilab 865 (see Mucci et al., 2010 for details), calibrated against the same CRMs used with the VINDTA.

In-situ pH_T, DIC (ArcticNet 2009 only), pCO₂, Ω_{c} and Ω_{A} , were calculated from TA and pH_T(25°C) or TA and DIC (for 548 out of 4730 data points) with the Excel - 2.1 version of the CO2SYS algorithm (Lewis and Wallace, 1998), using the carbonic acid dissociation constants determined by Mehrbach et al. (1973), refit by Dickson and Millero, (1987), the HSO₄⁻ dissociation constants of Dickson (1990) and the total boron concentration (B_T) from Uppström (1974) at the *in-situ* temperature and pressure. pCO₂ was normalized in CO2SYS against the mean temperature of the top 100 meters of the water column (-0.4 °C). The resulting ∂ pCO₂ / ∂ T/pCO₂ values range between 0.033 to 0.051 °C⁻¹, with a mean of 0.046 °C⁻¹, in good agreement with values obtained by Jiang et al. (2008; 0.027-0.042°C⁻¹) and Takahashi et al. (1993; 0.0423 °C⁻¹).

2.3.2 Quality control

In order to assess the robustness of the computed DIC values, we calculated DIC from TA and $pH_T(25^{\circ}C)$ and compared the results with the measured DIC values. The resulting coefficient of determination of the linear fit to the measured and calculated DIC values, R^2 , is 0.989, while the mean difference between calculated and measured DIC

values is ~2 μ mol/kg. We excluded 30 measurements that differed from the calculated values by more than 50 μ mol/kg (2.5% of the mean DIC).

Questionable TA measurements, excluded from the dataset, were identified as those outside a range of 3 standard deviations from the mean salinity-normalized TA for individual regions (CB, CAA, BB) characterized by internally consistent water mass assemblages. TA measurements obtained from the two instrumental methods (VINDTA and Radiometer Titrilab 865) used in 2015 and 2016 were also compared to ensure that data originating from both methods could be used interchangeably in the calculation of additional parameters and conjointly in time series. The resulting coefficient of determination between both datasets (R²) is 0.988, the mean of the non-systematic discrepancy between values is 6 µmol/kg and its maximum is 36 µmol/kg, respectively corresponding to 0.3% and 1.7% of the mean TA. The degree to which the results of this test are representative of the entire dataset is uncertain, but they constitute the best possible estimate of the uncertainty associated with the use of the two methods for measuring TA. When TA measurements obtained from both methods deviated significantly (>10 µmol/kg), specific alkalinity (TA/S_P), which should remain relatively constant in a given water mass of uniform salinity (Millero, 2005; p.268), was used to determine which data to discard. The deviation from TA values calculated from DIC and pH_T(25°C) was used to complement the first method, especially at the surface, although the validity of DIC measurements was previously assessed using TA.

2.3.3 Error estimation

In order to quantify the error associated with the calculated carbonate system parameters reported in this study, we used the CO2SYS program modified by Orr et al. (2018), which applies error propagation to instrumental and constant-related uncertainties. For simplicity, we report the mean uncertainty for each parameter (see table 2.2), as the variance is minimal within our dataset. We found the additional uncertainty associated with the unavailability of nutrient concentrations (P and Si) as input parameters in CO2SYS to be negligible (up to 0.0006 pH units, 1.5 μ atm pCO₂ and 0.006 Ω units, as determined using nutrient data where available). The uncertainty on Δ DIC_{Bio}, the biological contribution to temporal variations of the surface DIC pool, was calculated by applying standard error propagation to the procedure described in section 2.4.3.

2.4 Results and Discussion

2.4.1 Recent Observations (2014-2016)

2.4.1.1 Surface Observations

To characterize the recent state of seawater carbonate chemistry in the study area, we use data obtained in the late summers (August - September) of 2014, 2015 and 2016. Uncertainties for each parameter can be found in the Methods section (2.3.3). It is

important to note that the mean regional values we report for the Canada Basin may be skewed by the higher density of stations located along the Mackenzie Shelf, and that our sample size for Baffin Bay consists of only 6 stations. The mean 2014-2016 surface (< 10 m) values of practical salinity (S_P), TA and DIC in the Canada Basin (CB), Canadian Arctic Archipelago (CAA) and Baffin Bay (BB) are presented in table 2.3. Practical salinities considerably below 25 were mostly observed near the mouth of the Mackenzie River, with some in the Queen Maud Gulf (QMG). The discrepancy between SP and TA values observed in the CB/CAA and Baffin Bay clearly illustrates the change in water mass regime west of Lancaster Sound (see section 2.2), while DIC, which is strongly affected by biological activity, shows a less prominent spatial pattern. In all regions, surface-water pCO₂, of which we only consider data acquired over the top 5 meters of the water column in order to render it more indicative of gas exchange potential, was largely undersaturated with respect to the atmosphere, by as much as 150 µatm (figure 2.3). This suggests that the region as a whole acts as a net CO_2 sink during the summer, as Geilfus et al. (2018) observed in 2011. Ahmed et al. (2019) came to a similar conclusion based on underway pCO₂ measurements carried out in the CAA between 2010 and 2016, but reported consistent temporal fluctuations of summer sea-surface pCO_2 and ΔpCO_2 driven by sea-ice processes. The handful of locations exhibiting a positive ΔpCO_2 (pCO_{2SW} – pCO_{2air}; outgassing to the atmosphere) are located in the QMG and the transect between Banks Island and Cape Bathurst (figure 2.4), where the episodic upwelling of upper halocline water is well documented (Mucci et al., 2010; Tremblay et al., 2011).

The saturation state of surface waters (<10m) with respect to aragonite (figure 2.5) ranges from 0.82 to 2.03 (mean 1.26), 0.73 to 2.01 (mean 1.22) and 1.47 to 1.69 (mean 1.57) respectively in the CB, CAA and BB. Ω_A correlates well with S_P (r=0.79; figure 2.6), although the surface samples with the highest salinities (S_P ~32), collected in Baffin Bay, were not the most supersaturated. Recurrent undersaturated conditions (Ω_A < 1), potentially threatening to calcifying organisms, are found at the surface in two areas: the central Canada Basin and the Queen Maud Gulf. Such conditions have been well documented in the former (e.g. Robbins et al., 2013), and attributed mostly to the input of sea-ice melt, which lowers Ω_A by diluting surface waters and promotes CO₂ uptake (Yamamoto-Kawai et al., 2011). As of 2016, surface undersaturation with respect to aragonite was limited to the central Canada Basin and did not extend to its bordering continental shelf, where Ω_A remains near saturation (1-1.25).

In the Queen Maud Gulf, surface Ω_A values as low as 0.84 and 0.73 (±0.16) were observed in 2015 and 2016, respectively (most visible as the two minima in figure 2.6). Most of the surrounding samples were slightly undersaturated ($\Omega_A \sim 0.90$ -1.05). Both minima were associated with locally higher pCO₂ values (~429 and 438 ± 6 µatm) and practical salinities of 26.54 and 22.17. Two mechanisms, namely the decrease in the calcium (Ca²⁺) ion concentration and alkalinity via dilution by freshwater and the decrease of the CO₃²⁻ concentration concomitant with a decrease in pH, explain these saturation minima. The former process is self-explanatory and results from the documented increase in freshwater inputs by melting of sea-ice (Yamamoto-Kawai et al., 2009b) and increased river discharge (Déry et al., 2016). We estimate, based on a linear regression of surface

 δ^{18} O data against S_P, that upwards of 95% of the freshwater at the surface of the QMG in 2015 was of riverine origin (see Annex; section 5.1). Our dataset does not allow us to directly differentiate the contributions of air-sea gas exchange and biological activity (respiration) to the high pCO₂ observed at these locations. Nonetheless, the depth these samples (<5 m) implies some degree of equilibration with the atmosphere. Although the diurnal cycle of biological activity may play a role in the development of peaks in Ω , we rule out this mechanism for the case discussed above, as the 0.73 minimum of 2016 was observed in the early afternoon. Although the Ω_A minima represent significant undersaturation, the uncertainty on Ω_A computations (0.08 or 0.16 depending on the parameters used in the calculation; see Methods) blurs the saturation threshold in such a way that Ω_A values marginally below 1 might in reality represent supersaturated conditions, and vice-versa. It is important to note that, even without the influence of climate change, areas of high riverine discharge naturally harbor lower carbonate mineral saturation states. Thus, undersaturated conditions in the QMG and elsewhere might not solely result from the documented increase of freshwater inputs described above, but dilution by freshwater affects the degree of this undersaturation as well as its spatial and temporal extent.

Surface waters throughout the study area are supersaturated with respect to calcite, with Ω_{C} ranges (mean) of 1.34 to 3.25 (2.04), 1.21 to 3.29 (1.97) and 2.38 to 2.70 (2.52) in the CB, CAA and BB, respectively. Uncertainties on Ω_{C} values are on the order of 0.25-0.30, almost twice as large as those of Ω_{A} , due to the larger uncertainty of the calcite stoichiometric solubility product at 25 °C and S_P= 35 (Mucci, 1983).

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2.4.1.2 Mackenzie River transects

The Mackenzie River plays an important role in the biogeochemical cycles of the Beaufort Sea as it is a major source of freshwater and particulate matter to the area (Iseki et al., 1987; Emmerton et al., 2008). Three transects extending across the Mackenzie Shelf were visited in 2015 and 2016. Two of these originate offshore from the Mackenzie Delta (red and blue traces in figure 2.7), and one in Mackenzie Bay (green trace in figure 2.7). Across the delta transects (not shown), surface salinity increases from \sim 20 to \sim 25 while DIC and pCO₂ decrease to varying degrees, indicating either CO₂ loss to the atmosphere upon mixing or carbon uptake through photosynthesis promoted by the nutrient influx from the Mackenzie River. Conversely, practical salinity decreases from ~28.5 to ~25 (along with DIC) across the Mackenzie Bay transect visited in 2016 (figure 2.7). This feature, highly unusual in estuarine systems, likely results from a geographical migration of the freshwater plume, strongly influenced by wind patterns (MacDonald and Yu, 2006). The main channel of the river, which flows into the Mackenzie Bay, also typically receives less freshwater discharge than the channels transiting through the Mackenzie Delta (Brunskill, 1986). The salinity of the water at the surface of the bay (28.48) is above the mean surface salinity of the Canada Basin (27.52), implying that there is only a small or negligible fraction of sea-ice melt along the continental shelf, relative to the central CB. In turn, this salinity feature largely explains the offshore decrease in carbonate mineral saturation observed in every transect, as the change in Ω_A is not consistently correlated with what one would expect based on variations of pCO_{2SW}

and pH. Although Total Alkalinity data are scarce, they appear to vary consistently with salinity.

2.4.1.3 Water column observations

Depth profiles of pH_T , pCO_2 and Ω_A grouped by region (equivalent to water-mass regime) are presented in figure 2.8. We divided the broad Canadian Arctic Archipelago region into four sub-regions (see figure 2.2): the Parry Channel, the east-west channel extending from M'Clure Strait to Lancaster Sound, the Amundsen Gulf, the Queen Maud Gulf and the central CAA, which connects the QMG to the Parry Channel. The water mass structures are essentially the same as those described in section 2.2.

The most prominent feature in profiles of carbonate system parameters in the Canada Basin is the Upper Halocline Layer (UHL), a layer of water originating from the Pacific Ocean with a relatively lower pH due to its high metabolic CO₂ content (Shadwick et al., 2011). In 2014-2016, the UHL was characterized by a pH_T minimum of 7.82 \pm 0.03, a pCO₂ maximum of ~652 \pm 6 µatm and a Ω_A minimum of 0.75 \pm 0.16 in the central CB. This pH_T minimum migrates upwards from ~180 to ~ 140 meters as the UHL encounters the continental shelf west of M'Clure Strait but maintains its amplitude. The presence of such an acidified layer exacerbates the vulnerability of the planktonic communities in this area, as, in addition to the aragonite undersaturation found at the surface, Ω_A drops below one at depths of 100 to 125 meters or even less in the Canada Basin. As CO₂ naturally

diffuses or mixes from the UHL to the overlying waters and the combination of gas exchange and freshening continues to generate undersaturated conditions at the surface, the entire photic zone (where $\Omega_A < 1.5$) may acidify and become undersaturated with respect to aragonite at a much faster rate than that of other oceans. The shallowest subsurface aragonite saturation horizon we observe in the central Canada Basin was found at ~85 meters in 2014. Our data do not corroborate the interpretation of Wynn et al. (2016) that the upper boundary of the UHL is migrating downwards due to an expansion of the overlying Polar Mixed Layer (PML). The Ω_A crosses the saturation threshold back to supersaturation between 200 and 250 meters, where Atlantic waters become predominant, as evidenced by a +0.8 °C temperature maximum at ~500 m (in contrast to a temperature minimum of -1.5 °C in the UHL). Ω_A and pH_T remain above 1.3 and 8.05 in this layer, with respective maxima of $1.74 (\pm 0.16)$ and $8.17 (\pm 0.03)$ that generally coincide with the temperature maximum mentioned previously. The profiles presented in figure 2.8 do not extend to the bottom of the basin, but deep waters become undersaturated with respect to aragonite below ~2100 m (data from 2009).

The Amundsen Gulf and the western portion of the Parry Channel (Figure 2.8; CAA1) essentially exhibit the same water mass structure and carbonate system features as the Canada Basin, as the dominant circulation pattern pushes water eastward from the CB to the CAA. Undersaturation with respect to aragonite does not occur at the surface in these areas, owing to higher salinities. Although the amplitudes of the Ω_A , pH_T and pCO₂ excursions are slightly smaller than those found in the CB, the UHL is considerably

shallower in the western CAA. Consequently, Ω_A becomes undersaturated at depths of 50 to 70 meters, and the upper portion of the water column in those parts of the CAA might become undersaturated with respect to aragonite even more rapidly than in the CB. As reflected by the blue lines in figure 2.8 (CAA1), the UHL becomes progressively less visible on depth profiles as it undergoes modification and mixing during its transit from the CB to Lancaster Sound. Atlantic waters are found at the bottom of the water column in the Amundsen Gulf and Parry Channel. The saturation maxima found around 400 m ($\Omega_A \sim 1.1$ to 1.4) are significantly lower in these areas than at similar depths in the CB.

The shallow bathymetry of the central CAA restricts the eastern flow originating from the CB to the layer of Pacific water (UHL) and the overlying surface water. Ω_A is close to 1 at the surface and reaches a maximum of ~1.45 (± 0.16) at ~30 m, before dipping back below 1 between 50 and 75 m, like in other parts of the CAA. With the exception of one profile that exhibits a strong pCO₂ maximum of 685 (± 6.49) µatm as well as pH_T and Ω_A minima of 7.80 (± 0.03) and 0.76 (±0.16), respectively, at a depth 125 m, this UHL feature becomes less prominent in the central CAA. Degradation of settling organic matter (remineralization) might explain this exceptional peak of greater amplitude than those observed in the Canada Basin at Station 310 in September 2016. Stratification becomes significantly weaker in the shallow waters (20-100 m) of the Queen Maud Gulf (figure 2.8; CAA2), one of the areas with the strongest tidal mixing in the CAA (McLaughlin et al., 2004). The residence time of waters in this area might also be relatively high, due to its geographical isolation from the main channels of the CAA, possibly allowing more mixing to take place. The combined effects of low salinities from freshwater accumulation (mostly

from river discharge) and the efficient redistribution of CO₂ through mixing result in low carbonate mineral saturation states throughout the water column. The QMG is the only region in our study area where the entire water column is undersaturated with respect to aragonite, making it an ideal location to study the effects of such conditions on aragonitic organisms.

East of Barrow Strait, where a sill restricts the dominant eastward flow to the upper 125 meters of the water column (Bidleman et al., 2007), the water mass regime changes. With the exception of one profile that captures the Pacific outflow through the western portion of Lancaster Sound at station 301 (figure 2.8, BB, blue line), this change is clearly visible in profiles of carbonate system parameters in Lancaster Sound and Baffin Bay, where the upper 500 m of the water column is completely oversaturated with respect to aragonite at each of the visited stations. Although surface waters in Northern Baffin Bay are a mixture of multiple inputs from the CAA and the Arctic Ocean through Nares Strait, the warm and saline Atlantic water inflow from the Labrador Sea dominates the water-mass structure in the region and accounts for the high alkalinity of these waters relative to the CB and CAA (Münchow et al., 2015). In Baffin Bay, waters become undersaturated with respect to aragonite and calcite at depths of ~600 and ~1400 meters, respectively. The pCO₂ and pH_T increase and decrease proportionally with depth.

2.4.2 Time series

Of the 420 stations that make up our dataset, twenty-four were visited at least on two different years and match our comparability criteria. These criteria are: 1) the stations were sampled within 31 calendar days of each other (this criterion is not ideal since seasonality is highly variable and driven by complex sea-ice processes, such as ice break-up) and 2) the stations are located within a 5 km radius. The mean time difference and distance between comparable stations are 12 calendar days and 1.81 km, respectively. Eight were visited three times, the remainder were visited twice. Figure 2.9 shows the location of each of those stations and the time interval between their earliest and latest sampling years. With the exception of one site in northern Baffin Bay, all recurrently sampled stations are located within or on the outskirts of the CAA. Sixteen of the 24 time-series span 3 years or less. Within those stations, we identified the measurements made at similar depths in the top 100 meters of the water column (figure 2.10). The 2014-2015 and 2014-2016 intervals have the most comparable data points (~30), followed by the 2007-2009 and 2015-2016 intervals. The remaining year combinations have less than 10 comparable data points. The small data pool applicable to time series and the generally short and inconsistent time intervals between comparable data highlight the poor suitability of our dataset to the identification of temporal trends of ocean acidification. The strong variability of carbonate system parameters in the CAA strengthens this conclusion. Nonetheless, we use data from the seven stations visited over a time interval of at least 5 years (figure 2.11) to investigate any visible trends in

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carbonate system parameters. The resulting depth profiles are shown in figures 2.12 and 2.13.

To quantify near-surface change, we averaged data from the top 25 meters of the water column. Across this depth interval, between 2007 and 2016, the temperaturenormalized pCO₂, DIC and DIC/TA at site LS1 rose by $36 \pm 9 \mu$ atm, $37 \pm 10 \mu$ mol/kg and 0.008 \pm 0.005, while pH_T and Ω_A decreased by 0.042 \pm 0.037 and 0.12 \pm 0.23, respectively. Given its uncertainty, the change in Ω_A is insignificant. The same trend is visible between the same years at station CAA1, at a greater magnitude (+ 78 µatm pCO₂, -0.088 pH_T unit, -0.37 Ω_A unit), except for a DIC decrease of 58 µmol/kg caused by a decrease in salinity of 1.76. The DIC/TA, which effectively normalizes DIC against salinity, shows an increase of 0.021, proportional to the change in the other parameters. Data from the nearby station CAA2 also displays a similar trend between 2009 and 2015 (+ 29 µatm pCO₂, -0.041 pH_T unit, +0.001 DIC/TA), albeit a strong positive change in salinity (+1.81) contributed to an increase of 0.06 Ω_A unit (again, insignificant given its uncertainty of 0.23).

Four stations located on the transect extending from Cape Bathurst to Banks Island complete the seven time-series of at least five years (figure 2.13). Three of those time series (AM1, AM2, AM4) span 2003-2009 or 2004-2009. Thus, given their spatial and temporal proximity, we expect a certain consistency in the trends they exhibit. Surprisingly, salinity increased for each of the stations, by 1.46, 0.70 and 0.13, respectively. Despite the consistent salinity trend, stations AM2 and AM4 show opposite trends in carbonate system parameters, the former exhibiting a positive change in pCO₂

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 $(+49 \pm 9 \mu atm)$ and DIC/TA $(+0.010 \pm 0.005)$ as well as a negative change in pH_T (-0.089) \pm 0.037) and Ω_A (-0.20 \pm 0.23), while the latter displays negative but somewhat smaller changes in pCO₂ (- $35 \pm 9 \mu atm$) and DIC/TA (- 0.007 ± 0.005) as well as a positive change in pH_T (+0.051 ± 0.037) and Ω_A (+0.13 ± 0.23), mostly apparent near the surface (<10 m). The two profiles recorded at site AM2 exhibit a clear difference in stratification; a sharp peak in carbonate system parameters (associated with a temperature maximum) appears at ~ 25 m in 2003, while the top 50 meters were fairly uniform in terms of pCO₂, pH_T and DIC/TA in 2009. The magnitude of change in the carbonate system parameters at stations AM1 (2004-2009) and AM3 (2009-2016) is below their respective uncertainties. A relatively large change of -1.90 in near-surface salinity is observable at station AM3. The depth profiles of sites AM1 and AM3 (figure 2.13), both of which include measurements from three separate years, highlight the non-linearity of change (i.e. the variation between the earliest and the intermediate year is opposite from the variation between the earliest and latest years). Although this observation is limited to two groups of profiles, it constitutes a caveat to conclusions drawn from only two points in time.

Below 25 meters, variations in atmospheric conditions and biological activity become decreasingly influential on carbonate system parameters, relative to changes in water mass properties resulting from mixing. The largest change in our time series occurs at Station LS1, where pCO₂, DIC and DIC/TA increased by 265 µatm, 95 µmol/kg, and 0.040, and pH_T and Ω_A decreased by 0.140 and 0.38 over the 25-100 m depth interval, between 2007 and 2016. This drastic change reflects the varying proportions of Pacific and Atlantic Ocean waters that reach Lancaster Sound, the latter water mass intruding episodically into the CAA (Prinsenberg and Bennett, 1987). An increase in the abundance (or a change in the properties) of Pacific Ocean water between 2007 and 2016 is likely the cause of this feature, as a similar trend is visible at station CAA1, located east of Barrow Strait, where the intrusion of Atlantic Ocean water is halted by a 125-m sill. This is supported by the absence of a strong increase in salinity in Lancaster Sound in 2007, which would indicate a pulse of intruding Atlantic Ocean water. This feature is reversed at station CAA2 between 2009 and 2015, highlighting the interannual variability in the properties of the UHL. Below this layer, water properties are relatively uniform in time at stations CAA1, CAA2, LS1 and AM2, except for pCO₂ variations on the order of 20 to 30 μ atm. Station AM1 exhibits a strong change in deep water (300 to 400 m) properties between 2004 and 2008, the latter year seeing considerably less acidic conditions (+ 0.25 pH_T unit), while salinity and temperature profiles are nearly identical for the two years, suggesting vertical carbon export from the surface as a mechanism.

As previously stated, these time series present snapshots in time and cannot be assumed to represent the continuous evolution of the carbonate system in the Canadian Arctic. Nonetheless, even with a small sample size, we can confidently state that the temporal evolution of carbonate system parameters in the region does not display a systematic trend on sub-decadal timescales. Moreover, most of the significant changes our time series exhibit are associated to variations in the physical oceanography of the region (water-mass distribution and circulation) or surface processes (melting of sea-ice). Given the well-documented rapid melting of sea ice cover in the region (e.g. Tivy et al., 2011), we did not expect to observe increases in summer surface salinity over time intervals of 5 to 9 years. Our time series therefore offer proof of the strong interannual variability of this highly dynamic system. Discerning the ocean acidification signal amid the various physical and biological sources of change would require continuous time series over a longer period of time (see section 2.4.4 for a detailed justification).

2.4.3 The Biological Contribution to Interannual DIC variations: ΔDIC_{Bio}

We define ΔDIC_{Bio} as the change in the contribution of in-situ biological activity (photosynthesis and respiration) to the DIC of a parcel of water over a given period of time. ΔDIC_{Bio} is calculated for each depth at recurrently visited stations according to:

$$\Delta DIC_{BIO} = DIC_{Observed} - DIC_{Reference}$$

where DIC_{Reference} is computed in CO2SYS using the temperature-normalized seawater pCO_2 calculated at a reference time (from measured TA and pH_T) and the TA measured at the time of interest (the year for which Δ DIC_{Bio} is reported). The change in global mean atmospheric CO₂ concentrations between the reference year and the year of interest is added to the pCO₂ in order to account for gas exchange (data from Dlugokencky and Tans, NOAA/ESRL). This approximation rests on the assumption that the yearly increase in surface water pCO₂ follows that of the atmosphere (given stable biological production), as observations from global monitoring stations demonstrate (e.g. González-Dávila et al., 2010), although the validity of this claim is weakened on short spatial and temporal (subdecadal) scales (Fay et al., 2013, Wanninkhof et al., 2013). This also restricts our calculations to the upper portion of the water column (25 m) that is in direct contact with

the atmosphere. Under the additional assumptions that DIC is only affected by gas exchange, biological activity and mixing, and that TA is not significantly affected by biological activity (Zeebe and Wolf-Gladrow, 2001), DIC_{Reference} represents the DIC of a parcel of water if its *in-situ* biological component remained unchanged relative to a reference year (i.e., identical contribution, negative or positive, from the balance between photosynthesis and respiration). Because the reference pCO₂ is calculated in part from TA, changes in water masses should not affect the results of this analysis, given the salinity range of the data subset used in the calculation of Δ DIC_{Bio} (25.6 < S_P < 33.7). Thus, Δ DIC_{Bio} can provide insights into the interannual variability of biological activity in the Canadian Arctic, without direct measurements of parameters such as chlorophyll or biomass.

Figure 2.14 shows ΔDIC_{Bio} , averaged over the top 25 meters of the water column, at the 18 stations where comparable data were available, all located in the Amundsen Gulf and CAA. The magnitude of the calculated ΔDIC_{Bio} is beyond its uncertainty, which varies from 6.4 to 14.3 µmol/kg (mean of ± 8.6 µmol/kg), at 11 locations out of 18. All significant results from the month of October (2003-2009 and 2007-2009) in the Amundsen Gulf show a positive mean ΔDIC_{Bio} (a decrease in biological DIC uptake and/or an increase in DIC production) of up to 20.6 ± 10.5 µmol/kg. Conversely, the ΔDIC_{Bio} calculated for the month of August (2004-2009, 2009-2016 and 2014-2015) is generally negative and of a similar magnitude. Data from September are variable in direction and show the greatest change over consecutive years: relative to 2014, in the Amundsen Gulf,

the mean ΔDIC_{Bio} fluctuated in 2015 and 2016 by +28.0 ± 11.0 to -11.2 ± 8.0 µmol/kg over the 0-25 m depth interval.

It is unlikely that the consistent directions of change we observe for the months of August and October represent actual trends, given the small data pool and inconsistent reference states used to make those observations. Nevertheless, we can use this analysis to constrain the contribution of fluctuations in biological activity to the interannual variability of the DIC. In the top 25 meters of the water column, the maximum amplitude of ΔDIC_{Bio} is 45.9 ± 11.5 µmol/kg, observed in the Amundsen Gulf between 2014 and 2015. This maximum is not visible on figure 2.14, which only shows mean values. The Pearson correlation coefficient (r) between ΔDIC_{Bio} and ΔDIC (the change in DIC over the same time interval) is 0.52 and the associated coefficient of determination (R²) 0.27, suggesting that 27% of the interannual variability in surface DIC in the Canadian Arctic Archipelago is a direct result of the variability in biological activity. This has important implications with respect to the interpretation of DIC time series in the region and explains, in part, the long time of emergence of DIC as a proxy for acidification, compared to other carbonate system parameters, as discussed in section 2.4.4.

The extremely weak (r = 0.08) correlation between ΔDIC_{Bio} and the time interval over which it applies provides additional evidence of the absence of a trend in the balance between photosynthesis and respiration in the surface waters of the Canadian Arctic. The variability in this balance is driven by many interconnected, often localized processes. For

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instance, short-lived episodes of upwelling of halocline waters not only directly change the chemical properties at the surface, but also provide nutrients that stimulate biological activity (Tremblay et al., 2011). Primary production in the Arctic is also closely linked to the seasonal cycle of sea-ice (e.g. Arrigo et al., 2008). Beyond its natural fluctuations, ongoing disruptions to this cycle and other physical properties (stratification, temperature, etc.) forced by climate change are known to affect phytoplankton communities and their productivity (Ardyna et al., 2014; Blais et al., 2017), possibly increasing their imprint on the variability of DIC and other carbonate system parameters. As previously mentioned, variations in water mass composition cannot directly explain variations in ΔDIC_{Bio} . Nonetheless, mixing is likely accompanied by changing nutrient concentrations, which influence the balance of photosynthesis and respiration (Tremblay et al., 2015).

2.4.4 Time of Emergence of Ocean Acidification Signals

The time of emergence (ToE) of a process affecting a natural system is the time required for the measurable effects of this process to emerge from the natural variability of the system. The concept is predominantly applied in global climate change modeling studies, for which the results are either "years of emergence" based on a pre-industrial steady-state (e.g. Friedrich et al., 2012) or time intervals across which observations must be made in order to distinguish an anthropogenic signal from natural variability. Few of these studies use observations (e.g. Sutton et al. 2016), and, to our knowledge, none of them focus on the Arctic. The method implies the choice of a threshold in the forcing-to-

variability (or signal-to-noise) ratio, most often expressed relative to the annual or interannual standard deviation of the investigated environmental parameter.

Given the strong variability of carbonate system parameters in the Canadian Arctic, a largely coastal region that is poorly or not resolved in most Earth System models, estimating the region-specific time of emergence of the ocean acidification signal, in this case the minimal length of time series needed to observe its effects, is of primordial importance in the planning of effective research strategies.

We define the time of emergence according to the following equation:

$$ToE = \frac{C \times N}{S}$$

in which N is the natural variability, defined (after Hawkins and Sutton, 2012) as the standard deviation of the annual means of one of four parameters (DIC, T-normalized pCO₂, Ω_A , pH_T), across 7 years from 2003 to 2016. *S* is the slope (in units / year) of the theoretical acidification curve, constructed by calculating the evolution of a given parameter in CO2SYS, at a constant alkalinity (2000 µmol/kg), practical salinity (30) and temperature (0°C), and assuming that the surface ocean pCO₂ increases at the same mean rate as the atmospheric pCO₂ between 2003 and 2016 (data from Dlugokencky and Tans, NOAA/ESRL). Our computed rates of acidification (table 2.6) are in general agreement with the values reported by Bates et al. (2014). C is a constant that sets the threshold of emergence at either 2 or 3 standard deviations (N), i.e. when the acidification signal becomes significant beyond natural variability as it emerges from 95% or 99.7% of the observed annual mean values, assuming the data are normally distributed. Only data

collected at the surface (depth < 15m) from June to October, inclusively, are used to minimize the effect of seasonal variability.

Although the assumption of relative equilibration with atmospheric pCO₂ might be less applicable at these depths, we applied the same technique using data from depths of 100 m and 300 m in order to estimate the time of emergence below the surface, where the interannual variability should be relatively small.

The results of this analysis are presented in table 2.4. At the surface, pH_T and pCO_2 have very similar times of emergence of 23-35 years and 25-37 years for C values of 2 and 3, respectively. The Ω_A signal emerges after a slightly longer time, 31-46 years. The ToE of DIC is considerably longer than that of the three other parameters, at 118-177 years. The discrepancy with other parameters is largely due to chemical considerations, as the high Revelle factors (15-20) in the region imply that the change in pCO_2 caused by the uptake of atmospheric CO₂ will be 15 to 20 times larger than that of DIC, relative to their initial concentrations.

It is also important to note that distinct measurement techniques and their associated uncertainties create an analytical bias between different parameters, a bias that is not present in the same form in modelling studies. For example, although its analytical and computational uncertainties are relatively low, the non-systematic and sometimes large differences between DIC measurements of the same samples using two

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different instruments (see Methods, section 2.3.1) indicate the existence of an additional source of uncertainty that contributes to increasing its variability. The relative uncertainties of *in-situ* pH_T (0.3%) measurements and computed pCO₂ (4.5%) and Ω_A (6.4%) values are strongly correlated with their increasing times of emergence in the 0-25 m depth interval (r=0.88). Although this correlation becomes significantly weaker (r=0.49) when DIC and its relative uncertainty (0.4%) are included in the analysis, it suggests the presence of an analytical bias in our ToE estimates. Nonetheless, the similarity between the ToE of pH_T and pCO₂ as well as the large ToE of DIC are consistent with the findings of Keller et al. (2014).

Generally, we would expect the ToE of a given parameter to decrease with depth, as changing environmental conditions and associated biological activity normally lead to a stronger variability at the surface. In contrast, our results show a slight increase of ToE values from the surface to the 90-110 m depth interval (except for Ω_A that remains identical), followed by a decrease below surface values at the 290-310 m depth interval (except for DIC). Whereas a decrease of ToE from the surface to 300 m is expected, as noted above, the high values in the 90-100 m depth interval are anomalous. We attribute the relatively strong variability of the ToE in this depth interval to a periodical vertical migration of the upper boundary of the metabolic CO₂-rich (low pH_T, Ω_A , high pCO₂, DIC) Upper Halocline Layer (UHL) that is found at depths of ~100-200 m throughout most of the study area. Our results are also likely affected by the decreasing number of data with depth (table 2.5), which could lead to less accurate annual means and explain the increase of the DIC ToE from the surface to the 290-310 m interval.

Our results of ToE values for pH_T, pCO₂ and Ω_A are fairly similar those published in modelling studies under the same thresholds. Keller et al. (2014) report a ToE of 14 to 18 years for pH and pCO₂, and approximately 50 years for DIC in the Arctic. Rodgers et al. (2015) estimate a global mean time of emergence of the acidification Ω_A signal of less than 15 years (from 1950), using a threshold of one standard deviation (equivalent to less than 30 years with C=2). Henson et al. (2017) use a different approach to calculate that 25 years will elapse between the onset of the pH acidification signal and its emergence. Whereas Henson et al. (2017) note that ToEs in the Arctic Ocean are shorter than in other oceans, Keller et al. (2014) report the opposite. These contradictory results highlight the balance between the vulnerability of the Arctic to ocean acidification and the strong variability of physical and biological processes, both having opposite effects on ToE estimates. Although they are similar, our calculated times of emergence are consistently longer than those reported in modelling studies. This is consistent with the fact that coastal waters, that comprise a large portion of our dataset, exhibit a much higher variability in pH (and other carbonate system parameters) than open oceans (Duarte et al. 2013). Furthermore, direct observations are likely to integrate variability on temporal and spatial scales too small to be resolved by models.

Our observation-based time of emergence estimates suggest that, in the Canadian Arctic Archipelago and the coastal waters of the Canada Basin, 1) the ocean acidification signal will appear first in time series of pH and pCO₂, followed by Ω_A , and, considerably later for DIC; 2) without accurate measurements of the effects of biological activity and

sea-ice processes (both major drivers of natural variability), direct detection of the ocean acidification signal within a confidence interval of 95% will require at least 20-25 years of observations. Gathering data in the CAA in the next few years is critical, as regular shipbased observational campaigns in the region started in the early 2000's (Giesbrecht et al., 2014), implying the 20 to 25-year threshold would be reached in the next decade.

The validity of these conclusions depends on a methodology that differs considerably from its modelling equivalent, even if the results from both approaches are consistent with each other. In addition to the instrumental bias mentioned previously, our observations are subject to a sampling bias, since we only use data gathered in the summer months. The natural variability used in our TOE calculations therefore does not encompass the entire annual cycle. Nevertheless, because we define the natural variability of the system in terms of interannual rather than seasonal changes, the former should not change, assuming the amplitude of the seasonal cycle is constant through time. The other form of sampling bias possibly affecting our results is spatial, as cruise tracks and durations varied every summer.

2.5 Conclusions

Field observations of carbonate system parameters made between 2014 and 2016 in the Canadian Arctic reveal that surface waters of the region serve as a net CO₂ sink in the summer and are generally close to saturation with respect to aragonite ($1 < \Omega_A < 1.5$). Surface undersaturation ($\Omega_A < 1.0$) is found predominantly in the central Canada Basin, as documented in previous years (Yamamoto-Kawai et al., 2011; Robbins et al., 2013), and in the freshwater-influenced Queen Maud Gulf, the only area of the Canadian Arctic where the entire water column is undersaturated with respect to aragonite. The CO₂- rich Upper Halocline Layer creates a shallow aragonite saturation horizon at depths of 85 to 125 m in the Canada Basin and 50 to 70 m in the Canadian Arctic Archipelago, further fostering undersaturation near the surface and potentially threatening marine calcifying organisms living in this portion of the water column.

Time series of carbonate system parameters, although relatively short (<10 years) and incomplete in scope, illustrate the strong interannual variability of the region, due in part to complex circulation patterns and varied water mass assemblages. Our estimates of Δ DIC_{BIO}, the change in the contribution of biological activity to DIC, suggest that variations in biological activity (the balance between photosynthesis and respiration) account for approximately a third of the interannual variability of DIC measurements. Additional work must be carried out to extent this estimate to other carbonate system parameters (pH, pCO₂, Ω). Without direct measurements of biological productivity, the quantification of the progression of ocean acidification in the surface waters of the Canadian Arctic will require time series of 20 to 30 years for pH, pCO₂, Ω_A and much longer time series (>100 years) of DIC, based on the interannual variability of each of those parameters and the current rate of atmospheric CO₂ increase. Future work on ocean acidification in this region should focus on establishing continuous time series of carbonate system parameters, especially in areas where surface waters might soon

become undersaturated, as well as bridging the gap between observations of carbonate

mineral saturation and markers of ecosystem heath.

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Table 2.1: Research cruises carried out by the CCGS Amundsen from which

the dataset was constructed.

Cruise	Timescale
CASES	September 2003 - August 2004
CFL	September 2007 - July 2008
MALINA	July - August 2009
GEOTRACES	August - September 2009
ARCTICNET Leg 4a	October - November 2009
ARCTICNET	August - September 2013
ARCTICNET	August - September 2014
GEOTRACES / ARCTICNET	July – September 2015
ARCTICNET	August - October 2016

Table 2.2: Mean uncertainties of parameters computed in CO2SYS, their standard deviations and their relative weight with respect to the mean value of each parameter, for different carbonate parameter input pairs. * The ΔDIC_{Bio} uncertainty depends on whether $DIC_{Observed}$ was measured or computed.

Computed	Mean	Uncertainty standard	% of mean value		
parameter	uncertainty	deviation			
pH⊤(i-s)	0.026	0.002	0.3		
DIC	6.8	0.7	0.4		
(µmol/kg)					
Input Parameters: TA/pH⊤ (TA/DIC)					
pCO ₂	6.5 (25.0)	1.8 (6.7)	4.5 (17.5)		
(µatm)					
Ωc	0.27 (0.13)	0.04 (0.04)	6.5 (3.2)		
Ω_{A}	0.16 (0.08)	0.02 (0.02)	6.4 (3.1)		
	7.8-8.6*	1.3	69-77*		
(µmol/kg)					

Table 2.3: Mean surface-water (<10 m) practical salinity (S_P), total alkalinity (TA), dissolved organic carbon (DIC) and associated ranges in the three sub-regions of the study area in 2014, 2015 and 2016.

	SP		TA (μmol/kg)		DIC (µmol/kg)	
	mean	range	mean	range	mean	range
Canada Basin	27.52	19.11 - 30.82	2029	1820 - 2231	1929	1761 - 2066
CAA	27.57	22.17 - 31.40	1967	1604 - 2194	1868	1553 - 2061
Baffin Bay	30.96	29.69 - 32.10	2138	2062 - 2209	1999	1920 - 2058



Figure 2.1: Map of the study area with dominant surface circulation flow paths. After McLaughlin et al. (2004) and Proshutinsky et al. (2009). CAA: Canadian Arctic Archipelago.



Figure 2.2: Geographical location of the oceanographic stations covered by the dataset, color-coded according to the year of sampling, with the approximate boundaries of the main areas mentioned in the text.



Figure 2.3: Surface-water (<5m) pCO₂ and Δ pCO₂ (pCO_{2SW} – pCO_{2air}) from 2014, 2015 and 2016 in the Canada Basin, Canadian Arctic Archipelago and Baffin Bay. The blue, green and red dashed lines represent the average of the global mean monthly atmospheric pCO₂ values for August and September 2014, 2015 and 2016, respectively (data from Dlugokencky and Tans, NOAA/ESRL). The Δ pCO₂ axis shifts in accordance with the atmospheric value used for each year, such that points may be offset from their true position by up to 5.5 µatm.



Figure 2.4: Surface-water (<5m) pCO_2 in 2014 (top), 2015 (middle) and 2016 (bottom).



Figure 2.5: Surface-water (< 10m) Ω_A (left) and Ω_C (right) in 2014 (top), 2015 (middle) and 2016 (bottom). Note the different color scales for Ω_A and Ω_C , for which the diverging value for the former is 1, 2 for the latter.



Figure 2.6: Surface-water (< 10m) Ω_A and associated practical salinities (S_P, color scale) in 2014, 2015 and 2016. The horizontal line at Ω_A = 1 represents saturation with respect to aragonite.



Figure 2.7: (Left) Profiles of Practical Salinity (S_P), Total Alkalinity (TA), DIC, pH_T , pCO_2 and Ω_A at depths of 2 and 10 meters across a transect extending from the Mackenzie River out into the Canada Basin. (Right) Map of the three transects visited in 2015 and 2016.

Figure 2.8 (following page): Depth profiles of pH_T (left), pCO_2 (middle) and Ω_A (right) at representative stations of the Canada Basin (CB; top), Baffin Bay (BB; bottom) and the Canadian Arctic Archipelago (CAA). The latter is divided into 4 sub-regions (shown on figure 2.2): Parry Channel, Amundsen Gulf, Central Archipelago and Queen Maud Gulf (QMG).





Figure 2.9: Location and time interval between the earliest and latest sampling of recurrently visited stations.



Figure 2.10: Number of comparable data points in the top 100m of the water column, obtained from measurements made at the same station and within set depth intervals (of 3.5 meters at the surface, increasing progressively to 15 m to a depth of 100 m), between each year of the dataset.



Figure 2.11: Location of the stations visited over an interval of 5 years or more. Stations are designated by area-related acronyms (LS: Lancaster Sound, CAA: Canadian Arctic Archipelago, AM: Amundsen Gulf), that are not the station identifiers used during the expeditions.



Figure 2.12: Depth profiles of pCO_2 , pH_T , DIC, DIC/TA and Ω_A across time at one location in Lancaster Sound (LS1) and two locations in the Canadian Arctic Archipelago (CAA1,2).



Figure 2.13: Depth profiles of pCO_2 , pH_T , DIC, DIC/TA and Ω_A across time at four locations at the western limit of the Amundsen Gulf (AM1,2,3,4).



2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016

Figure 2.14: Mean ΔDIC_{Bio} (top 25 meters of the water column) at stations of the Amundsen Gulf (top) and Canadian Arctic Archipelago (bottom). The central dashed line (0) is the reference state, in relation to which ΔDIC_{Bio} is expressed (i.e. the point at the right extremity of a line indicates the ΔDIC_{Bio} relative to the year at which this line intersects the zero dashed line). The grey shaded area represents the range of uncertainty.

Table 2.4: Calculated times of emergence of carbonate system parameters at various depths, rounded to the closest year. The C value represents the threshold used (2 or 3 standard deviations of annual means).

Parameter		Time of Emergence (Years)		
		0 – 15 m	90 – 110 m	290 – 310 m
pH (i-s)	C = 2	23	26	21
	C = 3	35	40	31
pCO ₂	C = 2	25	36	20
	C = 3	37	55	29
ΩΑ	C = 2	31	31	20
	C = 3	46	46	29
DIC	C = 2	118	156	138
	C = 3	177	234	207

Table 2.5: Number of data points included in the annual means used in the time of emergence calculations.

Year	D		
	0 – 15 m	90 - 110 m	290 – 310 m
2003	166	30	15
2004	207	47	22
2007	65	24	10
2008	146	66	31
2009	103	17	10
2014	63	20	16
2015	24	10	5

Table 2.6: Values of natural variability (N; the standard deviation of the annual means of each parameter) and theoretical acidification rate (S; the slope of the theoretical acidification curve) used in the time of emergence calculations.

Parameter	Ν	S
pH (i-s)	0.025	-0.002 yr ⁻¹
pCO ₂	26.65 µatm	2.17 µatm yr⁻¹
ΩΑ	0.07	-0.004 yr ⁻¹
DIC	36.37 µmol kg⁻¹	0.61 µmol kg ⁻¹ yr ⁻¹

3. General Conclusions

As previously stated, the size and spatial distribution of the dataset used in this study made this project a timely opportunity to fill important gaps in the scientific literature pertaining to the carbonate system and ocean acidification in the Canadian Arctic, particularly in the Canadian Arctic Archipelago, a region much less studied than the Canada Basin. Within this context, the first knowledge gap to address is the lack of a thorough description of the current state of the carbonate system in the study area. The observations presented in this thesis, spanning from 2014 to 2016, provide such a fullscale picture, focused on the saturation state of seawater with respect to aragonite, an important proxy for ocean acidification that is directly relevant to the health of marine ecosystems. The most important conclusions of this portion of the project, highlighted in section 2.5, include the identification of two main zones where surface undersaturation with respect to aragonite is widespread, the central Canada Basin and the Queen Maud Gulf. Whereas the former region is the subject of a number of recent publications, information about the Queen Maud Gulf, where the water column is entirely aragoniteundersaturated, was lacking in the scientific literature. This characteristic makes this area a prime candidate for studying the effects of undersaturation on calcifying organisms in a natural high latitude setting.

In the interest of tracking the progression of ocean acidification in the Arctic, the second obvious use of a dataset spanning 2003 – 2016 was the construction of time

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series of carbonate system parameters. As detailed in section 2.4.2, this dataset did not lend itself well to this objective. Nonetheless, the resulting discontinuous time series provide insights into the variability of carbonate system parameters in the dynamic coastal environment of the Canadian Arctic Archipelago, that outweighs any temporal trends observed in the area. Fluctuations in biological activity account for a large portion of this variability, as estimated in the case of DIC (~27%). Large variations in carbonate system parameters also frequently result from changing water mass assemblages, particularly in the case of freshwater inputs from rivers and sea-ice melt. The comparative analysis of the interannual variability of pH, pCO₂, Ω_A and DIC and a theoretical acidification curve suggests that the ocean acidification signal will emerge from the natural variability of the system in time series spanning 20 to 30 years for the three former parameters and upwards of 100 years for DIC. Although the accuracy of these estimates is limited, they can be used to orient future research efforts in our study area.

Although the vast spatial coverage of the observations presented in this thesis adds to its relevance in the scientific literature, it presented a barrier to the amount of detail in which processes acting at smaller scales could realistically be investigated and described. The abundance of data in the Amundsen Gulf, for instance, could justify a more exhaustive analysis focused on this region alone. Some data that predates 2014, notably in northern Baffin Bay, did not appear in time series and was therefore overlooked. Furthermore, since the inception of this project, two research cruises have been carried out in the Canadian Arctic Archipelago by the CCGS Amundsen, in the summers of 2017 and 2018. Unfortunately, the data from these campaigns was not available in time to be incorporated into this work. Appending these data to the dataset presented in this thesis would provide much more spatially consistent observations from five or more consecutive summers in the Canadian Arctic Archipelago, allowing this study to be elaborated on. A collaborative study involving marine biologists should be undertaken in order to extract the most from of this work, as the effects of ocean acidification on marine Arctic ecosystems remain poorly understood.

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5. Annex

5.1 Estimation of the freshwater sources in the Queen Maud Gulf

In order to estimate the relative fractions of sea-ice melt and meteoric water (mostly river water) in the Queen Maud Gulf, we use δ^{18} O and practical salinity (S_P) data collected in the area in 2015 to perform a linear regression analysis. The methods of analysis of the oxygen isotopes, reported on the δ^{18} O notation (V-SMOW), is described in detail in Lansard et al. (2012) for the samples collected during the CASES expedition (2003-2004) and in Mucci et al. (2018) for the remainder of the samples.



Figure 5.1: Linear regression of δ^{18} O and S_P data from stations of the Queen Maud Gulf visited in 2015, with the associated trendline equation and coefficient of determination (R²).

Using the intercept of the trendline equation to extrapolate δ^{18} O to S_P = 0, we find the mean δ^{18} O of the freshwater found in the Queen Maud Gulf in 2015 to be -18.55. Based on the δ^{18} O values of meteoric water (-18.9 ± 0.1 ‰) and sea-ice melt (-2.0 ± 0.5 ‰) used by Lansard et al. (2012), the fractions of meteoric (river) water and sea-ice melt are respectively 98% and 2%. A potential source of error affecting this estimate is the use of the δ^{18} O of Mackenzie River water as the riverine end-member, which might differ significantly from the oxygen isotope signature of the rivers discharging in the Queen Maud Gulf.