The Northeast Greenland shelf as a potential late-summer CO_2 source to the atmosphere

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Abstract. The Northeast Greenland shelf ~~carbon system is largely undescribed with the exception of the region associated with the Northeast Water Polynya. We describe the carbon system and the dominant processes affecting it in the region between 24 August and 25~~ is a region currently considered to be an annual net sink of carbon dioxide (CO_2) from the atmosphere. Water from the Northeast Greenland shelf is advected to the formation regions of North Atlantic Deep Water and therefore any carbon uptake may be stored for ocean thermohaline circulation timescales. We present the most extensive study of carbon chemistry on the Northeast Greenland shelf to date made possible by opportunistic sampling due to a sudden decrease in sea ice concentration in late August and September 2017. ~~During this period the shelf was largely sea ice free and although the north shelf was a carbon dioxide sink, the rest of the shelf and slope acted as both source and sink. This is in contrast to the common perception for this Arctic outflow shelf region as a~~ These are the first full-depth measurements of total alkalinity and dissolved inorganic carbon at latitudes between 75 and 79 °N with additional data collected in the region of the Northeast Water Polynya and outside Young Sund. We find that surface mixed layer concentrations are variable and for many stations higher than the interpolated atmospheric concentration for the region during the sampling period. Below the surface mixed layer, CO_2 ~~sink during the ice-free season. In the southern end of our sampling area, and particularly along the slope, low values of TA can lead to the shelf being a strong carbon dioxide source~~ concentrations increase linearly with decreasing apparent oxygen utilisation. The mixed layer deepens during the study period which is associated with apparent changes in CO_2 uptake. The Northeast Greenland shelf is a hydrologically complex region with many processes influencing the carbonate system at smaller scales than our sampling density. The scatter in the dataset are more than mere outliers and their lack of relationship to any measured variable indicates a strong influence of currently undescribed process(es) or variable(s) at the sampled scales. These data were collected during a time of radically low sea ice concentrations for the region and may be an indication of future conditions. Since they indicate the potential of the region to act as a seasonal source of CO_2 to the atmosphere ~~. We hypothesize on the possible causes for this low TA~~ this may modify our current estimate of the region as a strong annual net sink relatively protected from the immediate influence of atmospheric warming and climate change.

1 Introduction

~~Since the 1990s, the~~ The Arctic Ocean and adjacent continental shelves are changing rapidly under the influence of climate

25 change (????). The Northeast Greenland shelf ~~has been determined to be an annual net sink for atmospheric carbon dioxide ()~~ ~~. This determination is based primarily on a few observations (????) and subsequent modeling efforts (?). ? used their data to develop the 'seasonal rectification hypothesis' which describes the region as~~ is an Arctic outflow shelf (??) and one of the two gateways (the other the Canadian Arctic Archipelago) through which water from the Arctic Ocean is transported southward into the North Atlantic Ocean (?). Together with the along-slope East Greenland Current (EGC), the shelf acts as a gateway

30 through which water from the Arctic Ocean can be advected to the Greenland Sea, the Irminger Sea, and the Labrador Sea, regions that are crucial to the Atlantic Meridional Overturning Circulation through the formation of intermediate and deep water masses (?). This means that any carbon stored in the region may be retained in the global oceans on the timescales of the thermohaline circulation (??). The consensus is that the Northeast Greenland shelf has been a net annual ~~sink . Their hypothesis is based on the concept that large primary productivity and sea ice melt cause the region to function as a strong sink~~

35 ~~of atmospheric carbon dioxide in spring and early summer. During autumn, prior to the region becoming net heterotrophic, the region is covered in sea ice which inhibits~~ carbon sink like other Arctic shelf regions, though this appears to be changing in response to changing conditions. The initial determination of the region as a sink was made through interpolation studies (?), Self Organising Maps (SOM, ?), and temporally and/~~limits the exchange of gases, including~~ or spatially limited observations using various methods, most focused on the Northeast Water Polynya or the near-coastal regions and fjords (????). Recent

40 studies have indicated the potential for the region to become corrosive in terms of aragonite saturaton (?) and highlight the difference between the carbon system on the eastern side of Greenland versus the west in terms of the relationship between carbon chemistry and depth (??). The latter is far more pronounced in western than eastern shelf areas and may be related to differences in their respective hydrography. Higher benthic production nearer to the shelf edge may be indicative of stronger primary productivity in this area, though the shelf is considered to be oligotrophic and the previously strong benthic-pelaic

45 coupling in the region may be weakening (?). Due to high sea ice cover during all seasons the shelf is challenging to access, making it difficult to consistently measure all the parameters required to determine the conditions and processes influencing dissolved CO_2 ~~, with the atmosphere. Since the uptake in spring and summer is larger than the release during autumn and winter, there is a net annual uptake~~ concentrations.

The northern North Atlantic and the Greenland Sea are more accessible and studies in these regions receiving water from the

50 Northeast Greenland shelf and EGC (e.g. ?, ?) show that waters sourced from the Arctic remain undersaturated in dissolved CO_2 while Atlantic waters can act as a weak seasonal source. Water from the North Atlantic that might be entrained into the EGC also tends to be undersaturated (??), but has rapidly increasing concentrations, particularly in Autumn below latitudes of 78 °N when concentrations are at or near that of the atmosphere.

The uptake of CO_2 ~~. More recently, the timing of the onset of seasonal sea ice cover in the Arctic Ocean is increasingly~~

55 ~~delayed and therefore it is unclear whether the seasonal rectification hypothesis still applies to the~~ gas from the atmosphere in the northern North Atlantic (>50 °N) is partially driven by the cooling of warm water at the surface during northward transport which increases gas solubility, including CO_2. High stratification and primary productivity in summer combined with deep convective mixing in winter enable the exposure of a more water to the atmosphere which further facilitates uptake. The Arctic

Ocean carbon system is less well understood due to low (spatial and temporal) sampling densities though the Eurasian Basin uptake of anthropogenic CO_2 is thought to be increasing (**?**). There are also additional processes at play in northern latitudes that influence CO_2 gas exchange, affecting both the solubility and biological pumps in the region such as the sea ice related processes of brine expulsion and sea ice melting, and the input of 10-11% of global meteoric river water (**?**). Each of these is characterised by their seasonality (**??**). The Atlantic Water being transported north into the Arctic (and into the EGC as part of the return Atlantic Current) is much warmer than it was in previous decades (**?**). This increase in heat has been associated with changes in the Arctic halocline which shields sea ice from melting from below (**?**) and is likely to also stimulate heating in the EGC and potentially the Northeast Greenland shelf ~~.~~

~~The Arctic Oceanis losing sea ice rapidly under the influence of Arctic amplification, i.e. the proportionally enhanced increase in Arctic atmospheric temperatures compared to those at lower latitudes (?). Atlantification of the Arctic ocean, the transport of warmer waterto higher latitudes, is co-occurring with atmospheric warming. Increased temperatures in both ocean and atmosphere contribute to sea ice melt which~~ where the warm surface water from the return Atlantic Current (RAC) comes in direct contact with sea ice advected from the Arctic Ocean. Since the RAC is a surface current this energy is directly available for the melting of ice (icebergs, melange, and sea ice). While the melting of melange and icebergs merely reduces the temperature and freshen the surface water, ~~in~~ changing the gas solubility, melting sea ice can release ikaite ($CaCO_3 \cdot 6H_2O$) which facilitates additional CO_2 gas dissolution (**?**). Reduced sea ice cover is thought to facilitate primary productivity through enhanced availability of light, providing nutrients are also available (**?**) and rates of net primary productivity are thought to be increasing (**?**) even in the face of increasing stratification and the associated nutrient limitation (**?**). The Arctic Ocean surface waters are nutrient limited (**?**) and the regions of extreme nitrate limitation are expanding, though primarily in the Western Arctic (**??**). As a result of surface water nutrient limitation primary producers are generally found under sea ice (**?**), in the sea ice marginal zone, particular where there is upwelling (**?**), or as a 'deep chlorophyll maximum' (DCM) below the nitrogen depleted surface layer (**?** and references therein). Since the DCM is not directly in contact with the atmosphere the ~~absence of energy available for mixing, enhances upper layer stratification . Increases in river runoff also add freshwater to the Arctic Ocean and control seasonal stratification in the long term (?).~~

~~Surface layer stratification can act as a double edged sword with respect to the carbon equilibrium between the surface mixed layer and~~ uptake by primary producers is not directly associated with drawdown from the atmosphere unless the strong stratification is broken and has a chance to equilibrate prior to sea ice freeze up. This equilibration needs to occur before the produced organic carbon is remineralised and before sea ice cover is extensive enough to form a barrier between ocean and atmosphere. This dominance of DCM may be a recent development. During the 1990s, primary productivity on the northern Northeast Greenland shelf was found near the surface in the Northeast Water Polynya and the required nutrients were associated with water from beneath the landfast and glacial ice (**?**). This led to the ~~atmosphere depending on the carbon chemistry of this layer. The chemistry is determined by the composition of advected water with local processes such as precipitation and sea ice melt and freeze processes superimposed. After initial losses of solutes during initial frazil sea ice formation, temperatures in the new congelation ice layer at the water surface are sufficiently cold for the mineral precipiate ikaite (··) to form. The crystals of ikaite formed are thought to be preferentially retained in the sea ice while the carbon continues to be lost through~~

Figure 1. (a) Overview of carbon system chemistry and CO_2 fugacity (fCO_2) samples on the Northeast Greenland shelf. Arrows indicate known major currents. White indicates the advection of Arctic and Atlantic water, including Return Atlantic Water (RAW), Polar Surface Water (PSW), and Eurasian Basin or Arctic Atlantic Water (EBAW/AAW). Black is the Northeast Greenland Counter current (NEGCC) which transports water west then northward in a counterclockwise direction directly past the coast, purple is the Greenland Gyre, and orange is the East Greenland Current (EGC) which roughly follows the continental slope. SOCAT surface water fCO_2 measurement coordinates from **?**, CARINA full depth carbon chemistry stations from **?**. Numbers 1, 2, and 3 refer to the Northeast Greenland Ice Stream (culminating in 79N glacier or Nioghalvfjerdsbrae and Zachariae Isstrom), Young Sund, and the Northeast Water Polynya region respectively. (b) Known sources of total alkalinity to the Arctic Ocean highlighting the source regions of the Transpolar drift (green area with dashed white outline) and the location of the study area (red rectangle). Sources to the Arctic Ocean include Arctic rivers with variable catchment geology, sea ice and snow melt, and the Pacific Water coming in through the Bering Strait. River TA values from **?**, Pacific from **?**, and Atlantic from **?**. Sea ice TA is from own measurements during these cruises **?**. Locally, there is an unknown contribution of both sub- and supraglacial sources as well as glacier-fed rivers. Bathymetry was sourced from IBCAO (**?**), sea ice extent from OSTIA (**?**), and ice velocity from QGreenland v2 (**?**)

95 ~~brine drainage (??). When this layer melts it could thus release this calcium carbonate as excess alkalinity, compared to the initial seawater the ice was formed from, to the water column directly below (?) and enhance~~ development of the 'seasonal rectification hypothesis' which describes strong uptake of atmospheric CO_2 ~~uptake. The enhancement of alkalinity may be further enhanced by the presence of snow at the sea ice surface in which this process seems to be enhanced (??). Usually this effect is considered to be small when considered mixed into winter mixed layer depths of 70 m (?). In a highly stratified environment with summer mixed layer depths of 10~~ during the sea ice melt season by primary producers followed by a season

100 of inhibited autumn CO_2 release to ~~30 m only, like on~~ the atmosphere by the development of an extensive sea ice cover (**?**). Since then, the open water fraction in the region has changed dramatically as has the temperature of the Arctic river influenced Polar Water layer (**?**). In the summer of 2017 the Northeast Greenland shelf experienced a sudden drop in sea ice cover starting in August 2017 initiating a previously unseen decline in Arctic Ocean sea ice export which persisted throughout 2018 (**?**). These ice-free conditions allowed unprecedented access to previously unstudied parts of the Northeast Greenland shelf (Figure

105 1 a). The observations for this study were made opportunistically in these suddenly ice-free waters and may offer some insight into the response of the CO_2 system on the Northeast Greenland shelf to an increasingly warm and ice-free Arctic.

2   Materials & methods

2.1   Cruise & hydrographical setting

Data for this study was collected during two cruises (DANA2017 and NEGREEN2017). The hydrography of the Northeast

110 Greenland shelf ~~in late summer, a meltwater lens at the surface might promote the ocean surface absorption of .~~

4

~~Simultaneously, sea ice melt and other meteoric freshwater inputs that are low in nutrients can inhibit mixing by increasing the amount of energy required for mixing, though this effect may not be as large on the Northeast Greenland shelf~~ during these cruises was described in our previous paper (**?**). To summarize briefly, several water types were found to be superimposed on much of the shelf albeit in different ways in different geographical areas. The hydrography is dominated by freshwater from various Arctic Ocean sources with different total alkalinity (Figure 1a) down to the depths of the Eurasian Basin Atlantic Water (EBAW) and Return Atlantic Water (RAW) which have similar practical salinities of respectively 34.8 and 35. The freshwater is primarily sourced from the Russian Shelf (particularly the Laptev Sea) where vast amounts of riverine freshwater are introduced changing the salinity and surface water geochemical properties.

This water is further geochemically modified in the Siberian shelf seas prior to cross-Arctic transport as a result of shallow bathymetry combined with high winds and extensive polynyas adding a measurable denitrification signal (**???**) and changing the isotopic fractionation (**?**). Finally the surface water masses are advected off of the Siberian continental shelves and entrained into the Transpolar Drift (TPD). Once entrained into the TPD the annual sea ice freeze-melt cycle will continue to freshen the ~~shoaling of the Atlantic Water layer (?). Once nutrients have been used up after the initial spring bloom, this stratification has the potential to inhibit primary productivity in the~~ surface layer by the export of brine and dilution with meltwater. This process diverts the slope of the surface water from that between Atlantic Water and meteoric freshwater toward the sea ice melt end-member in both TA-S and δ^{18}O-S diagrams. A comparison between the Laptev Sea and Northeast Greenland shelf in terms of apparent oxygen utilisation (AOU) against the nutrients phosphate and silicate, and nitrate to phosphate ratio, confirm the strong link between the Laptev Sea and the Northeast Greenland Shelf via the TPD. The surface water, located above the maximum Brunt-Väisälä frequency squared (N^2), and above the remnant of the winter mixed layer, is almost entirely depleted in nitrogen (median $NO_3^- = 0 \, \mu$mol/kg). Directly below this is a remnant of the ~~associated carbon drawdown from~~ winter mixed layer which exists at freezing temperatures and a practical salinity of ~ 31.4 psu ($\sigma_T \sim 25$). This is fresher than this inflection point was in previous decades (**???**). This layer contains, and apparently traps, the oxygen maximum indicating that it is not actively ventilated during the time when sampling occurred. From the salinity at the inflection point (and the oxygen maximum), there is a cold halocline layer which follows the freezing line up to a salinity of 34.0, the Lower Halocline Water. At this point we find another inflection away from the freezing line with a sharp temperature increase in temeprature to EBAW at 4 °C (S = 34.8) and AW at 6 °C (S = 35). The saltiest and warmest Atlantic Water found is likely sourced from the West-Spitsbergen Current. This water can be found at the surface just off the continental shelf and can make incursions onto the continental shelf, particularly further south. Surface conditions in terms of sea ice cover and surface temperature during the three weeks of the two cruises were variable (Figure 2) with warm surface temperatures and patchy sea ice dominating the first part, after which the sea ice fraction increased, particularly toward the north and north-west part of the ~~atmosphere. Carbon will continue to be formed and exported below the mixed layer as part of the productivity taking place in the deep chlorophyll maximum but due to being separated from the atmosphere will not be able to utilize atmospheric carbon, and rather use remineralised forms. During the polar night, light-driven autotrophy is not possible and the Arctic is considered to be net heterotrophic (?). If sea ice forms a cap across the ocean, mostly limiting heterotrophy-associated outgassing of , outgasssing is not sufficient to balance the large productivity seen during spring (and potentially summer and autumn) bloom(s). The later sea ice is formed, the more~~

Figure 2. ~~a: Known sources of total alkalinity to the Arctic Ocean highlighting the source regions of the Transpolar drift~~ Surface conditions ~~(green area with dashed white outline) and the location of the study area (red rectangle). Sources to the Arctic Ocean include Arctic rivers with variable catchment geology,~~ sea ice fraction and ~~snow melt, and the Pacific Water coming in through the Bering Strait. River values were taken from **?** and Pacific water from **?**. Locally, there is an unknown contribution of both sub- and supraglacial sources as well as glacier-fed rivers. b: CTD Stations and their associated TS-group~~ sea surface temperature) on the ~~Northeast Greenland~~ shelf and average mixed layer depth temperature per ~~? with the fraction of sea ice concentration on the 13th of September 2017 in red~~ station subdivided into four sampling periods. ~~Bathymetry was sourced from IBCAO (?),~~ ESA sea ice ~~extent from OSTIA (?),~~ surface temperature and sea ice ~~velocity~~ fraction were obtained from ~~QGreenland v2 (?)~~ **?** (**?**). Average station mixed layer depth temperatures are the average temperature for all sampled depths above the maximum Brunt-Väisälä frequency squared (N^2)

~~likely it is for heterotrophic outgassing of to start balancing out autotrophic uptake, leading to a lower annual net uptake of overall (?).~~

~~This paper focuses on describing observations made of alkalinity and dissolved inorganic carbon during late summer and early autumn of 2017. Since these observations were made during a period of low sea ice cover, they provide a possible insight~~
150 ~~into the response in terms of exchange on the Northeast Greenland shelfto a changing climate~~shelf.

3 ~~Materials & methods~~

2.1 ~~Cruise location and sample analysis~~

~~Data for this study was collected during two cruises (DANA2017 and NEGREEN 2017) (Figure 1). CTD stations were placed into groups based on their temperature and salinity characteristics, resulting in 5 groups that matched different geographical~~
155 ~~areas as shown in (Figure 1 b). These groups will be referred to as TS-groups since they are based on their *TS* profiles for the remainder of the document. For more detail regarding the cruises, CTD station data processing, stable water isotope ($\delta^{18}O$),~~

2.1 Sample Analysis

Descriptions for the analysis of the Conductivity, Temperature, and Depth (CTD) instrument data, nutrients, and total alkalinity ~~analyses, please refer to our previous paper, ?.~~
160 are included in the methods section of **?**. To analyse DIC, seawater samples were transferred from the CTD Rosette to gas-tight vials (12 mL Exetainer, Labco High Wycombe,UK), poisoned with 12 µL solution of saturated $HgCl_2$, and stored in the dark at room temperature until analysis. DIC was measured on a DIC analyzer (Apollo SciTech, Newark, DE, USA) by acidification of a 0.75 mL subsample with 1 mL 10% H_3PO_4 (Sigma-Aldrich, Saint-Louis, MO, USA), and quantification of the released CO_2 with a nondispersive infrared CO_2 analyzer (LI-COR, LI-7000, Lincoln, NE, USA). Results were then
165 converted from ~~mmol~~ μmol L^{-1} to ~~mmol~~ μmol kg^{-1} based on sample density, which was estimated from salinity and tem-

perature. An accuracy of ± 2 ~~mmol~~ μmol kg^{-1} was determined for DIC from routine analysis of certified reference material (A.G. Dickson, Scripps Institution of Oceanography, San Diego, CA, USA).

CTD ~~data~~ measurements of temperature and salinity were combined with the TA and DIC ~~were used~~ bottle data to calculate the ~~pCO2 using the model~~ pCO$_2$ using the program CO2SYS (**?**) ~~using~~ with the dissociation constants ~~of ?~~ k1 and k2 of **?** refitted by **?** and the hydrogen sulfite dissociation constant from **?**.

2.2 Mixed layer depth determination

~~Surface conditions on the shelf through the period of data collection. Top row shows sea ice conditions, bottom row is sea surface temperature. Representative dates from left to right are the start date of collection (24 August), mid-collection (13 September) and near-end of data collection (21 September). Both figures are obtained from ? (?). The increased spatial patterning is due to cloud cover during the first period and reliance solely on lower resolution data~~

~~To investigate the potential direction of gaseous transfer between the atmosphere and ocean it is important to~~ We estimate the depth of the mixed layer ~~since this is the layer where such interactions take place. There are many different ways to determine mixed layer depth and ours is highly simplified. For each CTD station for which carbonate data was available, the mixed layer depth was assumed to be less than 70 m since that is the average expected winter mixed layer depth in the Eurasian basin where much of our surface water is thought to originate (?). Above that depth we decided that convection is most likely to happen at depths shallower than the maximum Brunt-Vaiisala frequency squared~~ by determining that of the pycnocline through the determination of the maximum Brunt-Väisälä frequency (N^2) ~~at that station. This is somewhat plausible considering not only the temperature and salinity profiles, but also that the dissolved oxygen maximum is directly below this depth and providing evidence that gases are trapped at depths below this as described previously (?).~~ (**?**) for all stations with bottles taken shallower than 120 m depth. Our previous study indicated this would be a good proxy since the pycnocline acted as a barrier, trapping dissolved oxygen below it indicating that this water was not ventilated during the period of our study. The maximum N^2 was calculated for each CTD cast individually and depths varied between 1 and 30 m, with shallower depth closer to the coast and further north.

2.3 ~~Meteoric and sea ice melt fractions~~

~~The determination of meteoric and sea ice melt fractions for this dataset in the Northeast Greenland shelf is far from straightforward. Not only are there multiple sources of meteoric freshwater with different contributions to the alkalinity and to the stable water isotopic composition (δ^{18}O, δ^2H) but also due to processes taking place on the shelf itself. Even if the primary source location for the freshwater found on the Northeast Greenland shelf is~~

2.3 Normalisation of carbon chemistry bottle data

The bottle data were normalised by the application to the ~~Laptev Sea and the Lena river in late summer 2017 (?), processes such as sulphate reduction and denitrification of organic matter have the potential to change the alkalinity during cross-shelf transport~~

(?) prior to advection into the Transpolar Drift The three main sources (end-members)are shown in (Table ??) , where Atlantic water includes water in the Return Atlantic Current which is advected directly from the North-flowing West-Spitsbergen Current, as well as Arctic-sourced Eurasian Basin Atlantic Water (Figure 1). These have different associated end-member tracer values including for δ^{18}O, alkalinity, and salinity. The Meteoric fraction similarly includes end-members with different, and potentially seasonally variable tracer end-member values, including water from Eurasian rivers with different catchments and local conditions, glacial discharge, local glacier-fed rivers, and direct precipitation. The sea ice melt fraction tracer end-members also vary and in addition can have a broad range of salinities between first-year ice that has not experienced flushing with snow and surface ice melt, compared to multi-year ice which has seen one or more summers and can be completely fresh. data of a fitted polynomial. The polynomial captures the effects of both the sea ice melt and meteopric freshwater dilution. A full justification, including a comparison with more traditional normalisation techniques, is provided in the Supplement with this manuscript.

Water mass fractions are calculated according to a system of three linear equations (??, ??, and ??) and utilise two of the tracers shown in Table ??.

2.4 Modified Z-score

$$f_1 \cdot x_1 + f_2 \cdot x_1 + f_3 \cdot x_1 = x_{1,obs}$$

$$f_1 \cdot x_2 + f_2 \cdot x_2 + f_3 \cdot x_2 = x_{2,obs}$$

$$f_1 + f_2 + f_3 = 1$$

Because the mean is heavily influenced by the extreme outliers in these data, parametric methods are not representative. Non-parametric methods relying on the median are more representative. The modified Z-score is one such method, it relies on the Mean Absolute Deviation (MAD). Data are marked as outliers when the modified Z-score is larger than a value D. Our choice of D (1.5) is discussed in the Supplement.

where f is the fraction, x is the tracer, and obs is the observation from the field. The use of different tracer combinations has a large impact on the fractions calculated (Figure ??). This is related largely to a lack of knowledge of the end-member's seasonality and mixing history at any given time in any given point during transport rather than to measurement precision. The first column in Figure ?? shows how our data plots onto a triangle of points for each combination of end-members. The best result is obtained if the values for each end-member are unique and different at the scale of the other end-members. This presents an issue where the variables are salinity and total alkalinity since their three end-member diagrams for the end-members of Atlantic Water, sea ice melt, and meteoric freshwater, is close to a straight line (Figure ?? a). This leaves δ^{18}O-S (Figure ?? d),

3 Results and discussion

Based on previous studies, the region is expected to act as a sink for atmospheric CO_2. Periods of high drawdown are specifically thought to occur when the light returns in spring allowing for autotrophic production during phytoplankton blooms including under ice blooms (??), and δ^{18}O-TA (Figure ?? g)during upwelling events in the marginal ice zone (?). The release of CO_2 during the dark season, when no photosynthesis can occur and the region becomes (net) heterotrophic, is inhibited by extensive sea ice cover (?). This ice-covered period can be associated with CO_2 supersaturation (?). Autumn is a transition period between a summer highly stratified environment where light is available and is dominated by sea ice and meteoric freshwater flux, and for meteoric water (Figure ?? h), these produce similar fractions with a difference between them of only -0.02 ± 0.01. For sea ice melt (Figure ?? i) however, the predicted fractions are very different. The δ^{18}O-S predicting a far smaller brine (negative sea ice melt) fraction than that ccalculated using δ^{18}O-TA. It is not possible to determine which of the latter has a lower error associated with it since we do not know the precise history of the water measses measured. This is different than was found by ? who found sea ice melt to be predicted with a difference of 0.03 for most their data using salinity with TA versus salinity with δ^{18}O. Compared to our data where the difference in sea ice melt fraction using these tracers are a magnitude larger at 0.33 ± 0.1 (Figure ?? c)winter environment that is dark, unproductive, and influenced by sea ice growth and brine rejection. In the northern North Atlantic, autumn is associated with the breakdown of stratification near the surface due to higher wind speeds and storms. This pattern is repeated in the Greenland Sea where average wind speeds tend to increase during the period of this study (days of year 240 - 256, ?), and August and September are associated with increasing concentrations of dissolved CO_2 after a seasonal low in July (?).

The fall of 2017 had exceptionally low sea ice cover for the region (?), allowing unpecedented access to undersampled regions of the shelf. The parameters which usually explain most of the variability in carbon dioxide fugacity (fCO_2) in the ocean surface are temperature (T), salinity (S), total alkalinity (TA), and using δ^{18}O with either TA or Sp (Figure ?? i) 0.14 ± 0.04.

End member values used to determine water mass fractions. Meteoric water values for δ^{18}O and TA are those of the Lena river. Sea ice melt values for δ^{18}O and TA are from own measurements on the shelf

Salinity δ^{18}O (‰ VSMOW) TA (mol/kg) Sea ice melt [a] 2 -2.344 ± 0.746 204 ± 162 Meteoric [b] 0 -20.5 788 Atlantic [a] 34.9 0.32 ± 0.34 2267.33 ± 50

A comparison of different 2 end-member fraction calculations showing how much the choice of tracer can influence the fraction calculated for each end-member type. The mixing triangles are shown in the first column, meteoric fraction in the second column, and sea ice melt fraction in the third column. The coloured lines connect the different end-members of Meteoric (MW), Sea ice melt (SIM), and Atlantic Water (AW) masses. Green is AW - MW, blue is AW - SIM, yellow is MW - SIM

3.1 Salinity normalization of carbonate system measurements

To analyse changes in dissolved inorganic carbon (DIC). Gas solubility is expected to increase with decreasing temperature, change with salinity as a result of variable dissociation constants through their dependence on ion activities. With increasing TA, the fCO_2 is expected to decrease since these are the ions associated with increasing the ocean buffer capacity (?), and DIC is taken up by autotrophs during primary production and converted to organic matter. The data collected on the Northeast

Figure 3. ~~Variation~~ Carbon dioxide fugacity fCO$_2$ plotted as a function of ~~the measured carbon system parameters with~~ potential temperature (a), practical salinity (b) normalised DIC (c), normalised TA (c), and ~~their polynomial fit~~ with depth for shallower (e) and deeper waters (f). The ~~vertical~~ orange lines in a,b are the best fit line ~~at S=31.2 highlights~~ for the ~~remnant of the winter mixed layer water as described~~ median $\pm$ 200 fCO$_2$ for each step in ~~(?)~~ controlling variable. ~~Opaque~~ The median for steps in salinity is shown as the blue line where values included in the median calculation ($\pm$ 200) are ~~mixed layer data based on N^2~~ bounded by the grey region. Data with orange stroke in a,~~transparent values~~ b and in colour in c,d,e,f are ~~below~~ values with a modified Z-score of within D $\pm$ 1.5. The red line in (a,b) is the ~~mixed layer~~ modified Z-score data best fit

Greenland shelf in fall of 2017 do not clearly show the patterns expected (Figure 3). The data are scattered and outliers do not follow a discernable pattern with respect to salinity or temperature. Outliers occur during both cruises, in measurements from both labs, toward high and low TA and DIC ~~that are not conservative with salinity such as changes due to (de-) nitrification, sulfate reduction, ikaite precipitation and /or dissolution or primary productivity, the influence of salinity needs to be removed~~ from the data. Several approaches are commonly used in the literature. These are frequently variations based on the original formulation,

$$nX = \frac{X_{meas}}{S_{meas}} \cdot S_{ref}$$

where X is the variable to be corrected for, e.g. TA concentrations, and at different depths. There is no clear correlation between the outliers and any variable measured. We therefore have to surmise that at this time we are missing a (set of) variable(s) and/or ~~DIC, Sp is the salinity, and meas and ref subscripts stand for the field measurements and the reference value respectively. Later iterations include corrections for a TA estimated by linear regression at the point Sp = 0 (?), or correct for the calculated sea ice melt fraction (?). Each of these corrections has associated issues and errors and may not provide useful information, especially where there are multiple low salinity sources for TA such as shelf environments host to catchments with differing geology. Furthermore, the use of a reference salinity is arbitrary. Although there are more official description of what a reference salinity is (?), in the case of salinity normalisation they are generally chosen to be the highest salinity seen for the dominant watermass in a particular region. This makes any comparison between different geographical regions with a difference in most saline input and therefore chosen reference salinity for calculated values subject to bias. This complexity primarily impacts mixed layer depths (?) where the meteoric-influenced layer is highest. If these normalizations rely on other assumptions such as those underlying the calculation of sea ice melt fraction from δ^{18}O, any error in these assumptions will be propagated into any subsequent application using the normalized data~~ process(es) with which to describe the extreme values in these data, and we do not have sufficient justification to remove any of the outliers from the dataset. We cannot discard any data without a good reason to flag it as an outlier, and with this amount of variability in the dataset using linear correlations loses some efficacy. Mean values are not representative of the data therefore any attempt at statistical analysis necessarily relies on non-parametric techniques such as the modified Z-score.

285 ~~The processes controlling the water mass composition and the associated shelf salinity and alkalinity are complex. In addition, fraction calculations suffer from the ambiguities discussed in the previous subsection, therefore these data might best be normalized with respect to salinity by the simple removal of a polynomial-predicted value from the data, rather than attempting to correct for the assumed representative values for the Northeast Greenland shelf which contains such vastly variable sources in unknown relative quantities. For purposes of comparison and to choose the best representative method for~~

290 ~~the salinity normalisation of the carbonate system data, four different salinity corrections were applied (Figure ??~~ Using median values of fCO_2 for steps of each controlling variable (T, S, etc) rather than the mean and picking values for fCO_2 between which the correlation is to be made or using an extreme modified Z-score outlier flag ($> D=1.5$), a linear relationship can be established for temperature (Figure 3a). The ~~first (Figure ??a) is the direct application of the polynomial from Figure ??,~~

$$X_{pred} = X_{obs} - X_{poly} + X_{Sp,max}$$

295 ~~where pred is the salinity-normalised value estimated by the equation, obs is the observational data, poly is the value predicted by the polynomial according to the equations in Figure ?? a,~~ same method fails for salinity (Figure 3b) because the median fCO_2 follows a slightly polynomial shape which means the line is an overestimate compared to the values calculated from CO2SYS. The median and inter quartile range (iqr) for the mixed layer depth based on the N^2 are 410.49 and ~~$X_{Sp,max}$ is, in this case where the variable to be normalized is TA, the average TA measured at salinites larger than 34.9. This method~~

300 ~~therefore still relies on an arbitrary choice of reference salinity but it reduces the number of assumptions made about the data, and rather makes the assumption that the polynomial captures the water fractions. We compare the polynomial corrected values to the traditional correction according to Equation ?? (Figure ?? b), the sea ice meltwater fraction only correction (Figure ?? c), and the normalisation according to ? (Figure ?? d), none of which entirely remove the influence of salinity on the data. The only two normalisations which produce a result relatively free from any pattern with respect to salinity are the direct~~

305 ~~application of the polynomial (Figure ?? a) and the sea ice correction followed by the correction pioneered by ? (Figure ?? e), which in this case could be considered a correction for the input of meteoric water. The linear relationship with a slope close to 1 in (Figure ??f) between these two ways of normalising the data with respect to salinity show that these might be used interchangeably, particularly where no $\delta^{18}O$ data is available in a system dominated by the admixture of sea ice melt and meteoric water to Atlantic Water. Any correction method introduces bias in the resulting normalized data. We choose to use~~

310 ~~the simplest correction with the least assumptions in an effort to minimize this bias i.e. the correction using a fitted polynomial (Figure ??a).~~ 147.58 μatm, which is above the projected atmospheric value for the region of 395 μatm based on SeaFlux (?) though this is for the entire time period which may not be representative (Figure 4). If we divide further by time, the period before 10 September has a median 477.66 with iqr 201.96 μatm and after this date the median goes down to 367.89 with iqr 110.66 μatm. This indicates a change in conditions, either between the sampling period or the sampling locations where the

315 region turns from a source to a sink. For samples taken near the surface, the apparent oxygen utilisation is under 95% indicating either its use in biochemical processes, or the active ventilation of or mixing with waters with even lower dissolved oxygen

11

Figure 4. ~~Comparison between different ways of salinity normalising~~ (a) the ~~data~~change in fCO$_2$ with changes in apparent oxygen utilisation (AOU). ~~Normalisation using the polynomial from Figure ??a, traditional normalisation~~ (b),~~sea ice fraction correction~~ (c) ~~, meteoric water correction~~ fCO$_2$ changes with ~~TA calculated for S=0 per ?~~ date, coloured respectively by distance of station to Greenland and the EGC (d) ~~, sea ice correction first, then subsequent meteoric water correction (e), and a comparison between~~ Data in the ~~polynomial correction and the stacked sea ice and meteoric corrections for both measured carbon system parameters~~ mixed layer depth (~~f~~MLD) ~~.~~for each station by date

concentrations. In case of the former, this may also be responsible for the some of the higher concentrations in surface layer fCO$_2$ though we have no additional evidence to show active remineralisation.

4 ~~Results~~

320 ~~Comparison of the total alkalinity (TA) and dissolved inorganic carbon (DIC) in the top 150 m between the TS-groups shows some intriguing differences (Figure ??). Surface values of carbonate system parameters have a large variability, ranging between ~1800 mol/kg (Slope 2 and Main Shelf groups) and ~2300 mol/kg (Main shelf and Off Shelf groups) in TA and 1800 mol/kg to 2100 mol/kg for DIC. The median full depth pCO$_2$ for each TS-group is Off Shelf: 611.8, Slope 1: 513.17, Slope 2: 481.1, Main Shelf: 412.31, and North Shelf: 367.44 and for the mixed layer only: Off Shelf: 611.6, Slope 1: 504.7,~~

325 ~~Slope 2: 485.9, Main Shelf: 391.9, North Shelf: 358.4. Surface layer values are lower on average for each TS-group (column) with the most distinct difference between above and below the mixed layer (as determined by depth of maximum N^2) in the Off Shelf and North Shelf TS-groups. The broadest range of surface values is~~ One of the reasons that the relationships between fCO$_2$ and temperature and salinity respectively is unpredictable and highly variable is that water types with different histories found on the ~~main shelf where most measurements were obtained. Though much of the calculated p~~on the shelf~~is higher than~~

330 ~~the atmospheric partial pressure of the gas (> ~400 ppm.), extreme elevations are achieved where the TA to DIC ratio drops below 1 (bottom row in (Figure ??) . This seems most prevalent in the Slope 1 and Main Shelf TS-groups. The North Shelf (located in the Northeast Water Polynya region) has the lowest calculated average p~~Northeast Greenland shelf can have similar end-member values for certain parameters. For example, meteoric freshwater from the longer fjords has had time to heat up before being advected onto the shelf, with air temperatures in summer as high as 10 to 12 °C (**?**). Atlantic Water (AW) from

335 the return current also has temperatures of over 4 °C and a salinity of 35. Eurasian Basin Atlantic Water (EBAW) i.e. Arctic Atlantic Water that has circumnavigated the Eurasian Basin and lost heat is cold but has a salinity of 34.8. This is very close to AW salinity (34.8/35 = 0.99).

~~Observations for each group. First row shows TA with depth (a to e), second row DIC (e to i), and the last row TA against DIC. Colors represent p, opaque values are the mixed layer and the transparent values below the mixed layer.~~

340 **3.1**

Both TA and δ^{18}O are independently influenced by sea ice formation. Much brine is lost during initial sea ice formation, especially in 'latent heat' polynyas where frazil ice formation is dominant such as the flaw polynyas on the Siberian shelves in the source regions of the Transpolar Drift. Much TA will be lost simultaneously unless it is captured into the ice matrix where it may form the mineral ikaite (··)(?). Meawhile the δ^{18}O fractionates due to the heavier water being preferentially taken up into the ice matrix (?).

The δ^{18}O:TA is characterized by a triangular pattern between points The proportionality of the difference in TA between AW is similar to that in salinity, e.g. 0.98 for a EBAW TA of 2274 (?) and an AW TA of 2317 (?) but the 1, 2, and 3 (Figure ?? a,c) which is not found in % difference may be indicative of additional processes rendering TA non-conservative in this layer, diluted by a large volume. The region is also known for its small diameter (5 - 10 km) but deep penetrating eddies which offshelf can reach down to over 1000 m (???). With our sampling density which has distances between stations that are frequently over 30 km such features could create heterogeneous results for neighbouring station locations.

At depths below the surface mixed layer, as defined by the Brunt-Väisälä frequency squared (N^2), the AOU and fCO_2 are inversely correlated (Figure 3e). This ranges from the remnant of the winter mixed layer which is supersaturated with respect to dissolved oxygen, AOU > 100 %, and the δ^{18}O:DIC (Figure ??b, d). TA is considered to be conservatively mixed where DIC is not and median fCO_2 is lower than atmospheric values at 383.39 with an iqr of 130.40 μatm, to depths where AOU < 80 % and the data between point 1 and two are interpreted as falling on the Atlantic Water to meteoric water mixing line, where the data betweeen 2 and 3 are considered to represent meteoric to sea ice influenced water. The most extreme values of pare primarily associated the Slope 1 group and fall between point 1 and 3 with lower than average (by almost 200) TA compared to meteoric-influenced water and higher δ^{18}O. These data have either average or higher than average DIC.

Carbon system parameters plotted against stable water oxygen isotopic composition and coloured by group (a,b) and calculated pfor all data (b,d). mixed layer data are opaque. Higher and Lower pindicate relative values, concentrations in c are a wider range than in d. The grey lines in a and b are average TA (2006 63) and DIC (1933 54) for the Main Shelf group mixed layer only

3.1 Salinity normalized data

Salinity-normalized data can be used to determine dominant processes controlling the carbonate system (?) and whether these vary by group, geographical location, and/or nearby features. The Pearson's correlations between the pfor each group in the mixed layer and the salinity-normalized carbonate system parameters as well as several directly measured parameters are shown in (Figure ??). Immediately obvious is that δ^{18}O and meteoric water fraction are the exact (0.01) inverse of one another for each group as also shown in (Figure ??). What is surprising is that temperature has no to weak correlation to calculated pCO_2, particularly on the main shelf, and excludes temperature as a dominant control on the gas.

It is apparent that each group is distinct from one another particularly in terms of the measured and normalized carbonate system parameters, with an anti-correlation (negative) relationship between TA and pCO_2 that is strongest in the Off shelf group. The DIC shows the opposite trend with a very high correlation between DIC and pCO_2 in the Main and North Shelf areas where no other parameters seem to have any influence.

375 ~~In the Off Shelf water the TA and DIC are both negatively correlated to the pCO₂. This does not seem to be related to the Atlantic Water fraction present or any other known variable except for potentially it's geographic location, with the Off Shelf group pCO₂ showing a moderately significant anti-correlations to latitude and longitude. The Slope 1 group stands out~~ fCO_2 has a median of 453.32 with an iqr of 119.61 μatm. The maximum AOU corresponds with higher Chloropyll a fluorescence in the remnant winter mixed layer which indicates that the dissolved bioactive gas concentrations in this layer are at least partially

380 driven by the presence of a Deep Chlorophyll Maximum (DCM) (Figure 4a). While surface conditions were variable during the sampling period ~~in terms of the strongest correlations between the water mass fractions through salinity and δ^{18}O and pCO₂. Slope 2 data are primarily anti-correlated to negative sea ice melt fraction (insinuating a positive correlation with brine).~~

~~Pearson's correlation table for pfor any controls thought to be possible influences on pon the shelf. Each row represents a TS-group, each column the correlation to pCO₂. Strongest positive correlation is +1, strongest negative correlation is -1 and~~

385 ~~no correlation is 0. We consider moderate significance for values |0.5 < r < 0.75| and strong significance for values |r > 0.75|~~

~~Although relationships with latitude and longitude vary and are stronger along-slope than on the shelf itself, plotting the normalized data against latitude provides us with an approximate location for possible geographically constrained influences such as large glaciers and fjords or bathymetric features (Figure 6). It can be seen that above 79N within the Northeast Water Polynya, the TA in the mixed layer is average for the dataset however the DIC has several lower than average outliers.~~

390 ~~Conversely, Young Sound is associated with a peak in TA, as does the region near the exit of Dove Bugt which receives meltwater and ice from the surge-type glacier StorStrømmen, though this area also has some low values (Figure 6 a). The DIC is high on the slope (Slope 1~~ sea ice fraction ~~and~~ ~~2 TS-group) between 78 and 79 řN (Figure 6 b). Plotted against one another, salinity normalized values can be indicative of the dominant processes~~ temperature (Figure 2), the region off-shelf, to the east of the EGC, is generally associated with warmer temperatures and higher salinity, while waters across the shelf itself have

395 colder surface temperatures. Sea ice is most persistent in the north. The first part of the sampling period had warmer surface temperatures on the shelf ~~(Figure 6c). The highest mixed layer TA associated with Young Sund are steep even for dissolution and might be influenced by geology which can't be shown by this type of plot (Figure 6a). Both CO₂ uptake and release seem to be taking place with the latter associated with the North Shelf and possibly with primary productivity. Mixed layer waters in the Off Shelf group and the higher pCO₂ waters of the Slope 1 group just below the mixed layer are associated with the~~

400 ~~formation of though the dominant process causing the formation of the mineral remains elusive from this plot.~~ itself, especially in the south along the coast. This is associated with higher fCO_2, particularly at higher distances from the Greenland coast and smaller distances to the slope (EGC). During the sampling period, the surface temperature cools and the sea ice in the north becomes more consolidated. The fCO_2 during the later period are much lower and trend below atmospheric saturation, potentially indicating a seasonal shift (Figure 4b,c). The increasing Mixed Layer Depth (MLD) near the end of the study

405 (Figure 4d) could support this though this could also be attributable to another process such as the presence of a front.

4 ~~Discussion~~

Double normalised (sea ice fraction then salinity) TA (a) and DIC (b) data variation with latitude and one another (c) is TA against DIC. Contours generated by CO2SYS at a temperature of -2 ̊C and a salinity of 31 to approximate representative values for the surface mixed layer on the shelf. Transparent and opaque points are all data versus mixed layer only respectively. YS refers to Young Sund, DB for Dove Bugt which receives meltwater and ice from Storstrømmen glacier, NEW to the Northeast Water Polynya, and 79N to Nioghalvfjerdsbrae

3.1

The mixed layer is the depth available for possible source or sink behaviour with resepect to between atmosphere and ocean and, as determined by maximum N^2, is shown in (Figure ??)together with the mean pCO_2 found between the surface and this depth for each station. The stratification is highly variable and only partially explained by distance to the coast and/or slope. Average mixed layer pin bathymetrically connected regions such as Belgica Trough apparently decreases with decreasing distance to the coast which may reflect the influence of the known counter-clockwise surface current in this location (?). The region around the mouth of Young Sund similarly shows a possible cross-shelf trend in p. In the mid-shelf region between the southern Young Sund transect and Belgica Trough there are fewer patterns with values above and below atmospheric partial pressures present and in no discernible order although mixed layer depths are shallower toward the coast and thus can reasonably be expected to limit atmospheric exchange.

Figure 5. Maps showing the depth Measured concentrations of the mixed layer according to depth < depth N^2max pTA (a) and the paveraged across these depths DIC (b) compared to determine values predicted using the potential average release or uptake algorithms from **?, ?,** and **?** . Since NO_3^- concentrations were only available for the last two weeks of to the atmosphere during cruise, these are the time of samplingonly data shown for the **?** fit in (b)

Some assumptions are required to conceptually simplify the processes dominating the carbon system on the Northeast Greenland shelf and enable their analysis. Since these potentially introduce systematic errors, these will be discussed prior to discussing the data.

410 ### 3.1 Northeast Greenland shelf alkalinity

Alkalinity is considered conservative with respect to salinity in the open ocean. Therefore in an ideal 2 end-member environment, alkalinity is expected to vary linearly with salinity between a single ocean source and a single freshwater source providing the non-conservative constituents are negligible. The Northeast Greenland shelf receives water from many different freshwater sources, each of which can leave its own imprint on measured alkalinity values and would increase systemic error if not

415 addressed. Some of the alkalinity sources and processes are shown in (Figure 1The algorithms established by **?** to determine TA and DIC for the North Atlantic (surface layer) fit our data well for TA, albeit with a lot of scatter (Figure 5 a).

The alkalinity of a terrestrial freshwater source depends on its substrate and rate of weathering of (?). This , together with any subsequent biotic or abiotic changes, means each river that discharges from a different catchment can have a vastly different freshwater alkalinity end-member, as is certainly the case for the six largest Arctic rivers (?). Because the This is not entirely

420 surprising since the dataset used for the algorithm was in part obtained from measurements of the northern part of the Northeast

Greenland shelf ~~is one of only two major outflow regions of the Arctic Ocean, the other being the Canadian Arctic Archipelago, multiple sources can be expected to be present on the shelf.~~

~~Rivers also supply large volumes of terrestrial dissolved organic matter which can impact alkalinity by acting as a proton acceptor (?). In addition it can be photo-oxidized, releasing (?) though this effect may be small due to~~ (?). To determine the best fit for DIC, they removed values for nearshore waters proximal to riverine meteoric freshwater sources from the dataset due to those measurements being lower than the algorithmically predicted values. Our measurements are also lower than the values predicted using their algorithm even though they are not directly near a meteoric freshwater source (Figure 5 b). Similar linear regressions were fitted by **?** and **?**. The former do not provide an accurate reflection of our data and the second have a similar slope but a lower intercept. The **?** equation is therefore the ~~low solar angle at high latitudes. Contributions to alkalinity by (fluorescent and/or dissolved) organic matter can no longer be discounted (??), particularly where water masses are subject to production of fluorescent organic matter that is associated with sulfate reduction and enhanced alkalinity such as within the Chukchi shelf sediments (?). These sediments are already known to contribute to such signals as the denitrification-influenced nitrate to phosphate ratio, which is frequently used as a tracer for waters passing across these sediments (?, ; ?) and are also known to take place in other regions such as the East Siberian and Laptev Seas (?). River-associated coloured dissolved organic matter is present on the Northeast Greenland shelf (?) and is thought to play a role in heat absorption (?). Both heat absorption and any reducing processes within this layer or in its formation region may influence the carbonate system by decreasing gas solubility and changing the alkalinity.~~

~~Besides the aforementioned sea ice melt another potential cryospheric source of alkalinity is glacial discharge, with the largest contribution of the latter likely associated with marine-terminating glaciers that scour across beds with a high carbonate content. We do not at present have any direct measurements of individual Northeast Greenland glacier discharge alkalinity though much of the bedrock in this region is dolomite and is likely to contribute calcium and magnesium to runoff (?). The contribution to the total (titration) alkalinity from glaciers could also be low if it is sourced primarily from the supraglacial environment, e.g. snow, firn and/or ice melt that has not been in contact with bedrock since precipitation has an alkalinity of 0 and there are no known englacial alkalinity sources. A lot of the subglacial freshwater signal is thought to be lost fairly quickly during transport away from the source (??) and therefore any enhancement in alkalinity may be highly localized. We do have total alkalinity values measured in the glacier-fed rivers that are discharging into Young Sund (?) though whether the observed amounts of annual alkalinity contribution (e.g. 440 mol/year) is enough to explain the spike observed outside the fjord~~ best predictor for TA on the shelf~~and along the slope is uncertain 6~~.

~~We know that water on the Northeast Greenland shelf is subject to denitrification since this signal is frequently used as a tracer (?????). Denitrification can influence alkalinity (?) though this influence may be so small that it is negligible.~~

~~The geochemical signal of the meltwater from the Greenland Ice Sheet is small (1.8% at the glacial front according to **?**) compared to the volume of freshwater transported by the Transpolar Drift which is readily identifiable for example using coloured dissolved organic matter (?). If the different upstream sources of alkalinity (Figure 1a) are well mixed prior to their advection onto the Northeast Greenland shelf,they can be treated as a single source by determining the alkalinity of the combined sources from linear regression against salinity and solving the equation for a salinity of zero according to the second~~

~~equation in **?**. The shelf is highly stratified with a thin surface mixed layer that is heavily influenced by sea ice melt and freeze processes, and the TA:S plots are more appropriately fitted with a polynomial rather than a straight line from which a salinity of 0 may not give a combined meteoric source alkalinity for the water being advected from the Arctic (and/or North Atlantic) ocean.~~

3.1 ~~Regarding water mass fraction calculations~~

~~The use of linear equations to determine source fractions in Arctic ocean outflow regions is an increasing subject of debate. For example, **?** determined that sea ice brine and melt fractions sum to net zero across all the Arctic ocean exit gateways. When sea ice brine is formed, it sinks into the winter mixed layer or is transported even deeper through dense water cascading until it reaches a depth of neutral buoyancy (**??**). These brine-enhanced layers can be transported in a different direction and exit via a different gateway than the sea ice it was drained from and take different amounts of time even where they do leading to potential inter-annual and seasonal differences in fraction to the original water mass the ice formed from and resulting in a non-representative water mass fraction for sea ice melt and/or brine (fractions don't sum to 1). As a result, sea ice melt and sea ice brine cannot simply be assumed to be net zero within each individual region or gateway. The determination of melt and brine fraction therefore require a good understanding of the properties of~~ The difference between TA and DIC drives much of the fCO_2 variability calculated using CO2SYS, and increases (on average) between the first and second parts of the ~~water that these processes influence directly in their source region and season, rather than making inferences of a local balance at individual exit gateways at a given time~~

3.1 ~~TA and DIC on the Northeast Greenland shelf~~

~~Differences between our data and that collected in the previous decades are immediately apparent. Whereas previous studies classified the region as a CO_2 sink (**???**), our data show that at least during the period of our observations the area can act as~~ cruise (Figure 6a,b) as a result of a ~~CO_2 source, particularly in certain TS-group (Figure **??**). Previous studies focused mainly on the Northeast Water polynya dominated area, north of Belgica Trough and may not be representative for the rest of the shelf. South of Belgica Trough,~~ reduction in DIC. The average TA in the mixed layer remains the same throughout the study period. The reduction in mixed layer DIC relative to mixed layer TA is most pronounced at the lower latitudes in the ~~highest calculated pCO_2 fall below a TA to DIC ratio of 1:1 (Figure **??**k-o). This effect is particularly apparent for the Slope 1 group, although this pattern can also be seen in Main Slope stations. Although this is not the entire story with respect to these high calculated pCO_2 values, since the Off Shelf group shows the highest median pCO_2 across all depths, the mechanism whereby either TA is lost or DIC is gained across the shelf requires investigation.~~ southernmost transect near Young Sound (Figure 6 c).

3.1 ~~Alkalinity, meteoric water, and sea ice melt~~

~~One proposed mechanism for~~

Figure 6. (a) Mixed layer nTA/nDIC with depth for the surface mixed layer. (b) nTA and nDIC respectively by measurement date. Blue line is TA and orange line DIC best fit between 24 Aug - 10 Sep. Dashed lines are for dates after 10 Sep. (c) nTA against nDIC

As previously described in **?**, the original conclusion for the region being a CO_2 sink is the presence of large volumes of sea ice melt in the (surface) mixed layer. Generally the determination of sea ice melt fraction utilises the fractionation of $\delta^{18}O$ (**?**) or incorporation of TA (**?**) combined with a loss of salinity to the underlying water column during seawater freezing as a 3 equations with 2 known variable linear system. Further these two data can be plotted against one another (**??**) to differentiate between meteoric and sea ice melt influenced water in freshwater influenced Arctic shelves. Our data do not show the same clear relationships with lower pCO_2 in the Polar mixed layer and higher values deeper in the cold halocline layer, particularly enhanced in the Upper Halocline. In addition, their data do not show a similar triangular pattern in TA, missing an equivalent to our values between points 1 and 3 (Figure **??**a).

The anomalously low salinity-normalised TA in all TS-group except for the North Shelf group and high or average salinity-normalised DIC in the Main and North shelf TS-group are primarily responsible for the highest pCO_2 calculated (Figure **??** and **??**). Of course since these non-normalized data were used as inputs the calculated pCO_2 values are not independent.

We identified four possible drivers for these anomalies in TA:

1. Mixing with a secondary water source, either a freshwater source with a different TA for salinity = 0 or a secondary saline water source with a different TA for Sp > 34.9

2. Injection of brine into the system causing lowering of TA and increasing DIC

3. Biogenic calcification which decreases the TA while maintaining the same salinity.

4. Mixing with a water source that passes near/through an alkalinity titrating hydrothermal vent system which removes TA through the formation of $CaSO_4$

Mixing with a low TA water source would require the identification of a plausible water source. Glacial water with a lower (by 30 mol/kg) TA than DIC has been observed in West Greenland (**?**). The latitude of Young Sund, just north of the region of low TA, instead shows a spike in TA and Dove Bugt doesn't have values low enough to explain the observations. The Off Shelf water between latitudes of 74 and 75 °N could be a plausible source. Off Shelf water is characterized by the absence of a cold halocline layer (**?**) which means it it composed of Atlantic Water and surface water fractions. Neither of these are commonly associated with low TA therefore a biogeochemical change is still required before or after mixing (**?**).

The formation of brine as part of the seawater freezing process is expected to lower TA due to ikaite formation inside the ice, while losing DIC conservatively with salt. Most brine is rejected during frazil ice formation rather than in more consolidated ice, which loses more if it freezes more slowly. Although supercooling of several mK (**???**) has been observed in polynyas and therefore could hypothetically be cold enough to form ikaite crystals in open water, this has not been directly observed. Our normalised carbon system values (Figure 6c) do indicate a strong role for the formation of $CaCO_3$. This could be ikaite from

515 ~~a different source than sea ice such as through reactions of seawater calcium with sedimentary carbon as has been observed on an Antarctic shelf (?) however cold temperatures or high pH (?) are a pre-requisite for formation and therefore another mechanism may be more likely.~~

~~Extremely high primary productivity of calcium carbonate precipitating organisms can lead to a perceivable lowering of CaCO₃ without reducing salinity. Such lowering of TA with a stable salinity~~ depth-depedence of carbonate chemistry on the

520 Northeast Greenland shelf is non-linear. Whether the surface mixed layer will act as a sink or a source of CO_2 with respect to the atmosphere seems to vary though it is clear that the region is not as strong a sink as previously expected and may be a net source. Increases in freshwater, both meteoric as well as sea ice melt, are associated with more corrosive surface waters near the coast in the region (?) but this can be compensated for by high productivity stimulated by nutrient input from local ice melt (??). If this is the case this may be another reason for the extreme variability of results we obtained. The mixed layer

525 at the surface on the Northeast Greenland shelf that is advected in from the Arctic Ocean is already severely nitrogen depleted (?) which impacts opportunities for local primary producers to exist at the surface away from areas where local features such as eddies or actively melting sea ice might contribute nutrients to the surface water. Where sea ice melting, glacier melting, or potentially even iceberg fertilisation contribute nutrients to the surface, primary productivity can be quickly stimulated and the associated removal of DIC would allow for increased buffering by the TA and result in a lower fCO_2 in these areas. Sea ice and

530 iceberg melt can be patchy and major continental meteoric freshwater contributions directly onto the shelf happen primarily at the termini of the 79N glacier and Zachariaea Isstrom, therefore the extent of surface primary productivity influencing the carbon system is likely limited during the sampling period. The rest of the shelf receives local freshwater input from long fjords where all the nutrients added in the surface have likely already been fully utilised before they reach the shelf (?). This means that primary productivity is necessarily limited to a deep chlorophyll maximum (DCM) below the nitracline. During years of

535 more extensive sea ice cover primary production may occur closer to the surface and stimulate more direct uptake of CO_2 from the atmosphere. Higher benthic productivity has been observed ~~in both the red sea (?) and the Bay of Biscay (?) though never for the Arctic. The organisms that are generally associated with CaCO₃ formation include coccolitophores, foraminifera, and pteropods but may also include marine bacteria (?). Coccolithophores have been shown to thrive in regions where water from the Arctic Ocean mixes with Atlantic water (?) but their presence or absence cannot be verified by our data. A previous study~~

540 ~~of the primary producers in the region did not find any coccolithophores (?) though several different assemblages were found associated with the different water masses. The very warm water (up to 6°C) found in 2017 (?) was not present in their study.~~ closer to the EGC which, with strong benthic-pelagic coupling in the region, indicates higher productivity at the surface near the slope (?) and an associated higher uptake of CO_2. In the absence of sea ice melt it is possible that this is stimulated by along-shelf upwelling or by EGC-associated eddies which are particularly prominent in areas where the density of the warm

545 Atlantic and the cool Polar Water are the same (?).

~~Another mechanism that has the potential to lower alkalinity are the formation of CaSO₄ and the acidification of water through the increase in H⁺ associated with the percolation of water through hydrothermal vent systems (?). Two hydrothermal vent complexes were identified in proximity to our study area (?) and therefore these process cannot be entirely neglected~~

as playing a role though no sulphate or (trace) metal measurements were made during these cruises with which to draw this
550 conclusion.

4 Summary

4.1 Evaluating present state of the seasonal rectification hypothesis

Until the influence of warm ocean water on the melting of tidewater glaciers and ice streams became apparent (?) there were
limited primary source observations available for water on We present the first full depth carbon system observations of the
555 area of the Northeast Greenland shelf . Though bottle data (TA and /or DIC) samples were collected by cruises starting with
the USCGC Westwind (1979), USCGC Northwind (1984), USGC Polar Sea (1992), RV Polarstern (1993, 1999), and IB Oden
(2002), sampling for these parameters was limited. The first two cruises collected only between 75 and 79 °N, with additional
measurements outside of Young Sund and in the region of the Northeast Water Polynya. Our total alkalinity (TA) data to be
used as a tracer for sea ice (?). ? compiled and analysed TA and measurements correspond well to the predictive algorithm
560 created by ?, whereas the dissolved inorganic carbon (DIC) from 1992, ? used the 1999 cruise data to analyse the Redfield
ratio and presents only DIC measurements , and ? described both the TA and DIC from 2002. More recently TA and DIC
data for Northeast Greenland fjords were presented by ? who compared these with fjords along the western Greenland shelf
and concluded that high dilution by freshwater sources drives acidification inside the fjords. The coverage on the Northeast
Greenland shelf of these datasets is concentrated along Belgica Trough, within the Northeast Water Polynya, and along the shelf
565 edge and slope. The main shelf area has received comparatively little attention. Several ships have measured measurements are
lower than predicted by these authors. We find that the shelf does not act as a consistent sink as expected per the calculated
fugacity of carbon dioxide (fCO$_2$) from samples of TA and DIC. Using non-parametric methods due to the large number of
outliers in the dataset, we find that the surface of the region can act as either a sink or source of CO$_2$ directly, either by using
gas chromatography or underway infrared measurements. These can be found in the SOCAT database (?) but may not be easy
570 to compare to our data due to differences in results between TA/DIC and direct measurements where previously compared (?).

The general consensus from these previous studies is that the Northeast Greenland shelf is a sink though by how much is
still under debate (?). This is based on two concepts, the first of which is the seasonal rectification hypothesis which states
that the polynya experiences strong productivity driven drawdown in the open water season and is ice-covered once the system
575 becomes respiration dominated and would start to release to the atmosphere, and the second the idea that the shelf receives such
large volumes of sea ice and its melt that the (compared to DIC) enhanced alkalinity should enhance the uptake of atmospheric
CO$_2$.

Our data confirm that the North Shelf group mixed layer acts as a sink with respect to CO$_2$ though the region is not
representative of the rest of the shelf which shows high variability between stations. The North Shelf pCO$_2$ is driven by low
580 values of DIC rather than enhanced TA (Figure 6b) in the mixed layer so this likely reflects either CO$_2$ release or primary
productivity. In the mixed layer across Belgica trough the atmosphere. The highest uptake is associated with a maximum in

apparent oxygen utilisation (AOU) and chlorophyll within the remnant of the winter mixed layer where there is ~~a clockwise current toward the coast, there is a sequential decrease in pCO_2 with proximity to the coast (Figure ??b) that almost matches with a reduction in~~ both light and nutrient availability. This water is not actively ventilated and therefore cannot contribute directly to atmospheric carbon exchange. The middle of the study period saw an apparent breakdown in stratification based on an increase in mixed layer depth ~~from > 30 m to < 10 m (Figure ??a~~as determined by the maximum Brunt-Väisälä frequency squared (N^2). This ~~is also the region with the most persistent sea ice cover, which may be related to the thinning of the surface layer (Figure 2).~~

~~The Main Shelf mixed layer has an median pCO_2 value very close to that expected for the atmosphere and may act as either a source or sink interchangeably. Whether the Main Shelf acts as a source or sink depends on a combination of geographic location, eddies, wind fields, and other physical mixing mechanisms, and biological interactions that this study does not have the sampling density to identify.~~

~~The mixed layer along the slope is deeper than that on the inner shelf on average, and associated with that are higher median in calculated pCO_2 (Figure ??). Both the Slope TS-groups show that the impact of low TA is dominant in the calculated pCO_2 (Figure ??) compared to that of high DIC. In the case of the Slope 1 group this seems to be driven by strong physical mixing as shown by measured salinity and $\delta^{18}O$, and the calculated water mass fractions where for the Slope 2 group the highest correlation is with the calculated sea ice melt fraction. The Off Shelf group has the highest median values for pCO_2 in the mixed layer and is certainly a source to the atmosphere during September 2017.~~

~~The complexity that is shown by our dataset is much higher than could be anticipated by previous studies in the region. Our~~ was associated with a reduction in surface layer fCO_2 to median values below the expected atmospheric concentration, apparently due to a corresponding reduction in DIC. The many outliers in fCO_2, particularly in the surface mixed layer, are not clearly associated with any known process or measured variable. It is likely that the shelf is characterised by influences at smaller scales than the sampling density of this study. August and September 2017 ~~measurements occurred in exceptional circumstances since the summer was extraordinarily warm and had anomalously~~ were extraordinary in terms of low sea ice ~~. ? discussed that their surface (< 70m) & polar water total alkalinity values correlated with salinity, which ours do not. The proposed seasonal rectification hypothesis is still a contender for the North Shelf region, however there was no ice inhibiting CO_2 exchange with the atmosphere on most of the shelf while clearly the surface values acted as a source in multiple locations. Whether this is indicative of a change which occurred in the intervening decades, or predictive of a change yet to come is currently unclear and requires further study and monitoring. It may also simply be typical for the region during this time of year. Since we have such a dearth of measurements, it is impossible to determine how much of our measurements represent change.~~ cover, which was the reason that opportunistic sampling of this previously unsampled area could take place. Our results may therefore not represent a baseline for the region when ice covered but rather may act as an example of the response of the region to future increases in oceanic and atmospheric heat and reductions in sea ice.

~~Our data show a clear departure from previous measurements made on the Northeast Greenland shelf and put into question whether the region acts as a consistent CO_2 sink. Upstream modification to the total alkalinity (TA) of the water advected onto the shelf from the Arctic Ocean as a result in water mass source changes through a shrinking or expanding of the Beaufort~~

~~Gyre and it's freshwater retention may be responsible for some of the observed differences. Locally, much of the variability in the carbon system is located in the surface mixed layer on the shelf proper and modified through processes taking place both there and through slope and shelf edge interactions. Any additional detail such as from the influence of sea icemelt lenses or eddy formation require a higher spatial and temporal sampling density across more of the shelf. The timing and magnitude of respiration and the mixing of denser water masses with higher concentrations of DIC and/or lower concentrations of TA toward the surface are important in determining whether or not the region remains an annual source or sink with respect to CO$_2$. Many more direct observations of this region will be required to adequately validate this region as an annual net source or sink and provide a baseline by which to measure any future change. This determination will also require an understanding of the complex processes incluencing properties which are usually considered conservative but may change on the Northeast Greenland shelf, e.g. the TA.~~

Author contributions. The fieldwork component including taking samples from the CTD was performed by Thomas Juul-Pedersen, Johnna Michelle Holding, and Søren Rysgaard Marcos Lemes and Mikael Sejr performed the geochemical laboratory measurements for TA and DIC in their institutes respectively. Subsequent data analysis, writing of code, and initial drafting of the manuscript was performed by the primary author. Extensive feedback on first and second drafts of the manuscript was obtained from all co-authors.

Competing interests. The authors declare no competing interests.