ORCA – Online Research @ Cardiff

1   **The biogeochemical impact of glacial meltwater from Southwest Greenland**

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47

48 **Abstract**

49   Biogeochemical cycling in high-latitude regions has a disproportionate impact on

50 global nutrient budgets. Here, we introduce a holistic, multi-disciplinary framework for

51 elucidating the influence of glacial meltwaters, shelf currents, and biological production on

52 biogeochemical cycling in high-latitude continental margins, with a focus on the silica cycle.

53 Our findings highlight the impact of significant glacial discharge on nutrient supply to shelf

54 and slope waters, as well as surface and benthic production in these regions, over a range of

55 timescales from days to thousands of years. Whilst biological uptake in fjords and strong

56 diatom activity in coastal waters maintains low dissolved silicon concentrations in surface

57 waters, we find important but spatially heterogeneous additions of particulates into the

58 system, which are transported rapidly away from the shore. We expect the glacially-derived

59 particles – together with biogenic silica tests – to be cycled rapidly through shallow

60 sediments, resulting in a strong benthic flux of dissolved silicon. Entrainment of this benthic

61 silicon into boundary currents may supply an important source of this key nutrient into the

62 Labrador Sea, and is also likely to recirculate back into the deep fjords inshore. This study

63 illustrates how geochemical and oceanographic analyses can be used together to probe

64 further into modern nutrient cycling in this region, as well as the palaeoclimatological

65 approaches to investigating changes in glacial meltwater discharge through time, especially

66 during periods of rapid climatic change in the Late Quaternary.

67

68 **Keywords**

69 Biogeochemistry, nutrients, glaciers, primary production, silica cycling

70

71 **Highlights**

72 - Novel multi-disciplinary approach to tracing freshwater and particle transport into
73   boundary currents;
74 - Significant glacial inputs reach coastal waters and are transported rapidly offshore;
75 - Low surface water dissolved silicon concentrations maintained by diatom activity
76   despite strong glacial and benthic supplies.

77

1. Introduction

The high-latitude regions are experiencing some of the most rapid environmental changes observed globally in recent decades. This is particularly true for the Arctic. Here, temperatures are rising twice as fast as the global mean, the Nordic Seas are warming at an accelerated rate (Alexeev, Walsh, Ivanov, Semenov & Smirnov, 2017), Arctic sea-ice is thinning and moving faster (Lindsay & Schweiger, 2015), and multi-year Arctic sea-ice is declining (Maslanik, Fowler, Stroeve, Drobot, Zwally et al., 2007), with significant implications for the interaction between the atmosphere and the oceans (Provost, Sennéchael, Miguet, Itkin, Rösel et al., 2017). The Greenland Ice Sheet (GrIS) is experiencing significant mass loss largely through surface melting but also via ice discharge at glacier fronts (Enderlin, Howat, Jeong, Noh, Van Angelen et al., 2014; Felikson, Bartholomaus, Catania, Korsgaard, Kjær et al., 2017; van den Broeke, Box, Fettweis, Hanna, Noël et al., 2017). This melting is likely to have a global impact: the North Atlantic receives freshwater from the Nordic Seas, GrIS, and the Canadian Arctic (Bamber, Tedstone, King, Howat, Enderlin et al., 2018), which influences the density structure, circulation, and stratification in regions where deep water-masses form; these represent a major component of ocean circulation that drives global fluxes of heat and freshwater (Carmack, Yamamoto-Kawai, Haine, Bacon, Bluhm et al., 2016; Proshutinsky, Dukhovskoy, Timmermans, Krishfield & Bamber, 2015; Yang, Dixon, Myers, Bonin, Chambers et al., 2016). In addition to freshwater budgets, there has been increasing focus on the role of glaciers and ice sheets in supplying organic material and inorganic nutrients to marine systems. There are significant fluxes of nutrients in GrIS runoff both in dissolved and particulate form, including nitrogen (Wadham, Hawkings, Telling, Chandler, Alcock et al., 2016), phosphate (Hawkings, Wadham, Tranter, Telling, Bagshaw et al., 2016), dissolved silicon (Hawkings, Wadham, Benning, Hendry, Tranter et al., 2017; Meire, Meire, Struyf, Krawczyk, Arendt et al., 2016), and iron (Bhatia, Kujawinski, Das, Breier, Henderson et al., 2013; Hawkings, Wadham, Tranter, Raiswell, Benning et al., 2014). The extent to which these nutrients reach the coastal oceans, and are subsequently advected or mixed from the continental shelves into the open oceans via boundary currents, is poorly constrained and a matter of debate (Hopwood, Bacon, Arendt, Connelly & Statham, 2015). Both dissolved nutrient and particulate dynamics are significantly impacted by circulation processes (Hopwood et al., 2015) and biological activity within glacially-influenced fjords. These regions could be a significant trap of dissolved

110   inorganic phases (Meire, Mortensen, Meire, Juul-Pedersen, Sejr et al., 2017), and have the

111   potential to prevent the nutrient-rich glacial waters reaching the coastal seas. Despite this

112   possibility, distal summer phytoplankton blooms have been detected off Southwest

113   Greenland in association with glacial melt (Arrigo, van Dijken, Castelao, Luo, Rennermalm et

114   al., 2017) and ecosystem models indicate sensitivity to meltwater input (Oliver, Luo,

115   Castelao, van Dijken, Mattingly et al., 2018). An understanding of how natural resources –

116   including fisheries, bird, and mammal stocks that are essential for food and encouraging

117   tourism – will respond in the future to increasing anthropogenic stress on a regional and

118   global scale relies on an understanding of foundational processes of these ecosystem

119   services, including marine biogeochemistry and the sources and sinks of essential nutrients

120   (Berthelsen, 2014; Meire et al., 2017; Weatherdon, Magnan, Rogers, Sumaila & Cheung,

121   2016).

122   The overarching goal of the Isotope Cycling in the Labrador Sea (ICY-LAB;

123   icylab.wordpress.com) study is to understand the cycling of nutrients in the climatically

124   critical but understudied regions of the Labrador Sea and Greenland fjords. The approach of

125   ICY-LAB is to capture the whole biogeochemical system in these areas of marked

126   environmental change using carefully planned field sampling strategies, with research

127   expeditions to coastal Greenland and the open ocean Labrador Sea. The principal dataset

128   was collected during an oceanic expedition on the RRS *Discovery* (DY081, July-August 2017),

129   with the aim to investigate the influence of glacial meltwater on nutrient cycling in the shelf

130   seas off SW Greenland. Particular focus was placed on the silica budget and how this is

131   framed within the oceanographic and biological processes acting on the W Greenland

132   margin. Uniquely, we combined a range of both traditional and novel methodologies to

133   detect and trace meltwater and glacial material from the shelf across the slope, and to

134   investigate the biogeochemical and biological impact of these inputs. Bringing these

135   different approaches together is essential in these margin environments to obtain a full

136   picture of biogeochemical cycling, providing a robust insight into the system over a range of

137   spatial and temporal scales that are otherwise challenging to resolve (Figure 1).

138

2. Methods and materials

2.1.   Fieldwork rationale

The data presented in this paper were collected during expedition DY081, centred on

the coastal shelf and slope regions off Southwest Greenland. Model results indicate that this

region is influenced by surface meltwater from the Western GrIS, in addition to a significant

input of freshwater delivered from the Eastern GrIS via the strong East Greenland Current

(EGC) (Luo, Castelao, Rennermalm, Tedesco, Bracco et al., 2016). The study locations were

selected to represent this conduit to the open ocean for glacial runoff from the Western and

Southwestern GrIS, which have been the focus of recent terrestrial studies carried out in

collaboration with the Bristol Glaciology Centre (Hawkings, Hatton, Hendry, de Souza,

Wadham et al., 2018; Hawkings et al., 2017). Full details of the oceanographic setting are
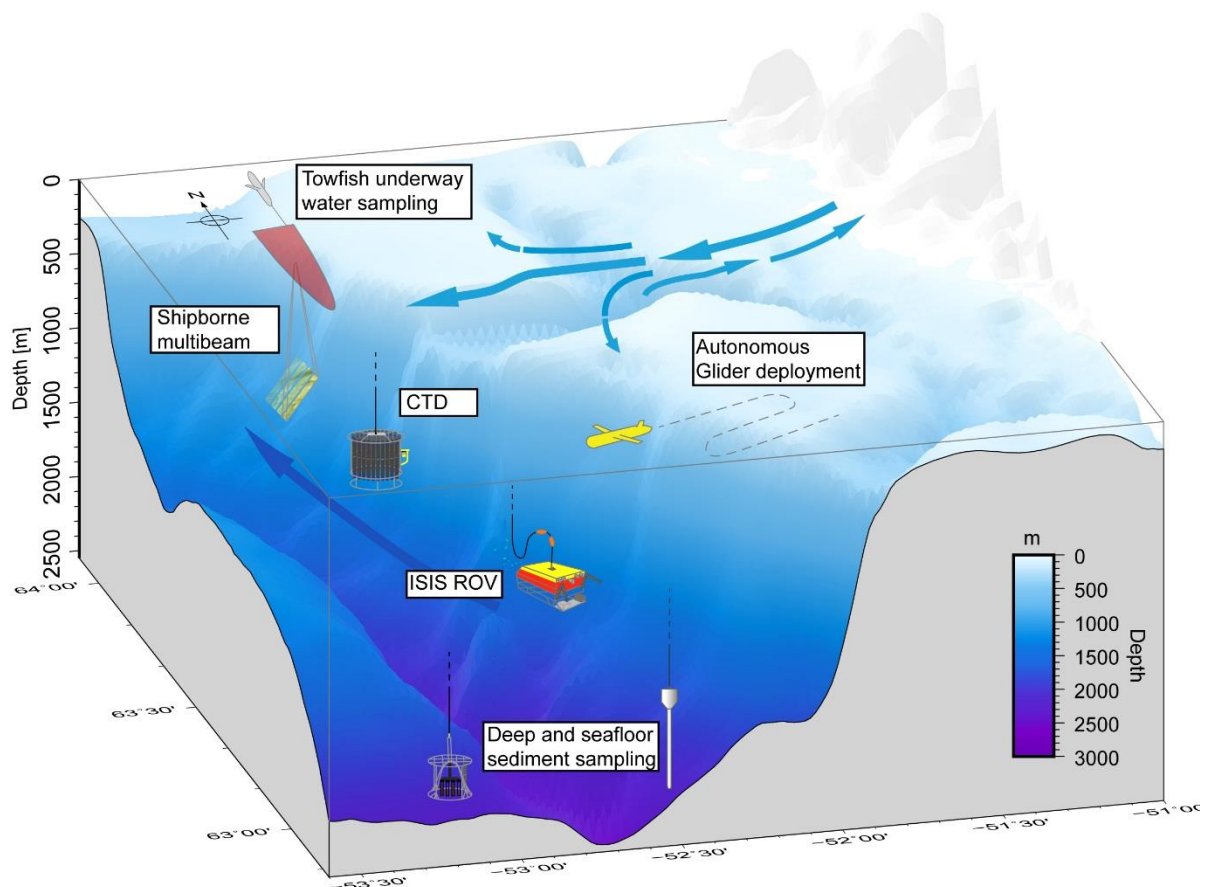
given in Appendix A.

Figure 1: Summary figure showing the multi-discipline approach taken during expedition DY081 of project ICY-LAB.

153   We selected the main study location for the ICY-LAB project ("Gothåb (Nuuk) Trough",

154   Figure 2a) to be adjacent to Nuuk, which has experienced increasing glacial run-off in recent

155   years (Van As, Andersen, Petersen, Fettweis, Van Angelen et al., 2014). During DY081,

156   Southern Greenland was strongly influenced by both icebergs and sea ice, but two sites

157   ("Narsaq" and "Cape Farewell", Figure 2a) were still selected there for providing glacial

158   troughs that could act as direct comparisons to the further north Nuuk site further north.

159   Orphan Knoll, on the western margin of the Labrador Sea, was selected as a distal

160   comparison site, and for complementary palaeoclimate, biological and habitat mapping

161   studies (Figure 2a).

Figure 2: A) Map showing route and main working areas of expedition DY081. Produced in Mercator projection with a standard parallel of 55˚N. Arrows show the main current systems in the Labrador Sea: Irminger Current (IC in yellow), West and East Greenland Currents and Labrador Current (WGC, EGC, LC in blue), and the Deep Western Boundary Current (DWBC). Cold, deep polar overflow waters are represented by the purple arrow. The main site of deep-water convection is marked by C, and represented by white arrows. B) Map of Nuuk grid location with ship track, bathymetry and station locations. Produced in Mercator projection with a standard parallel of 63˚N.

162

163   The unique holistic observational approach we took is illustrated in Figure 1, and

164   included (a) initial bathymetric mapping using acoustic methods (multibeam echosounders)

165   to increase our understanding of the local terrain and to enable accurate planning of further

166 sampling activities; (b) characterisation of the water column structure using CTD casts and

167 glider deployments; (c) sampling of surface and bottom waters for biogeochemical analyses

168 using the CTD rosette and a trace metal clean towfish; (d) sampling of seabed sediments

169 using a megacorer (for geochemical studies of pore waters) and gravity corer (for

170 palaeoceanographic investigations); (e) seabed observations and precision sampling for

171 biological, palaeoceanographic and sedimentological studies using a work-class scientific

172 ROV.

173

174 **2.2.   On-board methodologies and additional laboratory techniques**

175 *2.2.1. Mapping and acoustics*

176 During DY081, multiple acoustic systems were deployed on the ship (e.g. EM122

177 multibeam echosounder (12 kHz); EM710 multibeam echosounder; SBP120 sub-bottom

178 echosounder (2.5 – 6.5 kHz)). These were coordinated via a K-Sync system to avoid

179 interference and crosstalk.

180 Bathymetry data were processed on-board with the Caris HIPS & SIPS software v.8, using

181 standard settings and procedures (data import, navigation and attitude check, application of

182 a "zero tide", gridding into a 25 mx25 m pixel BASE surface). Backscatter data were

183 processed with Fledermaus FMGT, again using default settings.

184

185 *2.2.2. Physical oceanography*

186 High-resolution water column studies surrounding the prominent glacial Gothåb (Nuuk)

187 Trough were carried out utilising both a grid of Conductivity Temperature Depth (CTD) casts

188 and the deployment of two 1000m-rated Slocum gliders (Figure 2). CTD casts were also used

189 at the south Greenland and Orphan Knoll study sites. Hydrographic analysis enabled

190 characterization of the water column structure in each study location, specifically to locate

191 and quantify the freshwater inputs at the Greenland sites. Salinity was calibrated using

192 bottle samples collected at discrete depths. After laboratory calibration of these samples,

193 no drift corrections were required. Overall errors for temperature were 0.0006 °C (based on

194 laboratory calibration) and 0.002 for salinity. Prior to analysis, data from these stations were

195 gridded to a vertical and horizontal resolution of 10 m and 6 km respectively.

196 Vessel Mounted Acoustic Doppler Current Profilers (VMADP at 75 and 150kHz; Teledyne

197 RD instruments) were secured onto the drop keel in surface waters near the centre-line and

198 beneath the *RRS Discovery*, and used to measure the horizontal current velocity profile.

199 Bottom tracking data were only collected from the 150 kHz instrument intermittently

200 between 18th July and 24th July 2017 while close to Nuuk. In addition, downward and

201 upward looking lowered 300 kHz ADCPs (LADCPs) were mounted on the CTD rosette. LADCP

202 data were processed using LDEO LADCP processing software version IX_8, run on Matlab.

203 Full details of the other sensors attached to the CTD rosette and gliders can be found

204 elsewhere (Hendry, 2017).

205

206   *2.2.3.   Biogeochemistry and chemical oceanography*

207   *2.2.3.1.   Water column*

208   Water column samples were collected using Niskin bottles attached to the CTD

209 rosette (10L volume) and the Remotely Operated Vehicle (ROV) *Isis* (4 L volume), and via a

210 trace-metal clean towfish. The towfish system comprised of a weighted titanium bodied fish

211 lowered into the water at the stern and streamed as far from the ship as possible. When

212 towed it was at approximately 2m depth, and water was pumped into the ship's labs

213 through an ultra-clean pump and tubing. Trace-metal sampling was only carried out when

214 the ship was moving at speeds greater than 0.5 knots in order to avoid contamination from

215 the hull of the vessel. Four stand-alone pumps (SAPs) were also deployed at key locations to

216 collect water column particles.

217   Samples of seawater were collected for inorganic macronutrients, water oxygen

218 isotope composition ($\delta^{18}O$) and carbonate chemistry parameters (pH, alkalinity), which are

219 used for investigating freshwater input in high-latitude regions (Hendry, Pyle, Barney Butler,

220 Cooper, Fransson et al., 2018; Meredith, Brandon, Wallace, Clarke, Leng et al., 2008;

221 Thomas, Shadwick, Dehairs, Lansard, Mucci et al., 2011). Phytoplankton pigments were

222 analysed on board, and compared to sensor-derived fluorescence data, to assess algal

223 standing stocks in relation to meltwater input. Full details of sampling methods and

224 laboratory techniques are available in Appendix B.

225

226   *2.2.3.2.   Diatom productivity*

227   Biogenic silica ($bSiO_2$) production (i.e. diatom productivity) analyses were done using

228 radioisotope [32]Si as detailed in Krause, Brzezinski and Jones (2011). Briefly, samples were

229 collected within the euphotic zone (sample depths based on light and relative to irradiance

230   just below the surface) and dispensed into acid-cleaned 125 mL polycarbonate bottles. 322

231   Bq of $^{32}Si(OH)_4$ was added to each sample, and bottles were incubated on deck in surface-

232   seawater-cooled incubators covered with neutral density screening to mimic the depth of

233   collection. After incubation, samples were filtered through 1.2 μm pore size polycarbonate

234   membrane filters. Particulate ^{32}Si activity was quantified using a GM-25 Multicounter (Risø

235   DTU National Laboratory, Denmark) after the samples had aged into secular equilibrium

236   with the short-lived daughter isotope, ^{32}P.

237

238   *2.2.3.3.   Radium isotopes*

239   To investigate the fate of solutes sourced from benthic sediments or glacial meltwater,

240   large-volume surface samples for radium (Ra) isotope analysis were collected from the

241   trace-metal clean towfish system, both when the ship was underway (~2m water depth) and

242   stationary (~5m water depth). A total of 200-300 L of seawater from a single sampling event

243   were then passed through a plastic column holding MnO_2-coated acrylic fibre, which

244   quantitatively binds Ra in the sample. The fibers and adsorbed Ra isotopes were then rinsed

245   with deionized water (Milli-Q, Millipore), dried to an appropriate moisture content and

246   loaded into a Ra Delayed Coincidence Counter (RaDeCC; Scientific Computer Instruments,

247   USA) so as to quantify ^{223}Ra and ^{224}Ra content following the methods of Moore and Arnold

248   (1996) and Moore (2008). Each sample was counted 4 times over ~4 months to determine

249   the activities of excess ^{224}Ra and ^{223}Ra, above the activities supported by their parent

250   isotopes in the water column (^{228}Th and ^{227}Ac, respectively). Detector efficiencies were

251   determined and monitored regularly at sea and in the laboratory with standards (Annett,

252   Henley, Van Beek, Souhaut, Ganeshram et al., 2013). Final reported activities have been

253   corrected for any decay that occurred between sample collection and analysis, activity

254   supported by parent isotopes, detector background, and efficiency.

255

256   *2.2.3.4.   Sediment-water interface*

257   High-latitude ocean margin sediments are increasingly being recognised as an

258   important source of inorganic nutrients and key elements (Henley, Jones, Venables,

259   Meredith, Firing et al., 2018; Kuzyk, Gobeil, Goñi & Macdonald, 2017; Sherrell, Annett,

260   Fitzsimmons, Roccanova & Meredith, 2018). To investigate the role of sediments in these

261   glacially-influenced shelf and slope environments, we collected pore-fluid samples at coastal

262 Greenland and the Labrador Sea. Short sediment cores (≤40 cm) were acquired from the

263 study area with a mega corer. Using Rhizon filters (0.15 μm, Rhizosphere Research

264 Products), pore water was extracted from the sediment cores and filtered into syringes, and

265 the samples were stored under cool conditions prior to analysis. Pore water dissolved silicon

266 concentrations were analysed on-board and post-expedition using a V-1200 Vis

267 spectrophotometer, employing a standard molybdate-blue methodology (using Hach Lange

268 reagents). The samples were corrected for blank and calibrated against a ten-point curve

269 that was developed using Si standards of known concentrations. In addition to mega-cores,

270 we also employed ROV push cores to obtain short sediment cores for pore-fluid sampling, in

271 regions where complex bathymetry or the presence of ice-rafted material precluded the use

272 of a megacorer.

273

274 *2.2.4. Palaeoclimate*

275 Two samples types were collected for palaeoclimate research – fossil deep-sea corals

276 and sediment cores. ROV operations were the primary tool for benthic biological and fossil

277 coral collections using grab or suction devices. In addition, where large fossil coral

278 graveyards were observed, a net was used to sample fossil corals. Gravity cores were also

279 collected to obtain long-term records of changes in meltwater flux and iceberg dynamics

280 over the Late Quaternary, thereby providing a longer-term temporal context to the broader

281 data set. Megacores, collected primarily for biogeochemical studies, were also subsampled

282 to provide core-top material that could potentially replace any sections lost from the gravity

283 cores during retrieval.

284

285 **2.3. Mass balance calculations**

286 To calculate the freshwater mass balance in the study area, the seawater samples are

287 presumed to comprise a mixture of three source water end-members: ocean, sea ice melt

288 and meteoric water, which is assumed to be dominated by glacial discharge. The three end-

289 member assumption enables quantification of the freshwater fractions via the following

290 mass balance equations (Meredith, Heywood, Dennis, Goldson, White et al., 2001):

291

292 $$F_{ir} + F_{me} + F_{si} = 1$$

293 $$F_{ir}S_{ir} + F_{me}S_{me} + F_{si}S_{si} = S_{ms}$$

11

294
$$F_{ir}\delta_{ir} + F_{me}\delta_{me} + F_{si}\delta_{si} = \delta_{ms}$$

295

296 Where F_{ir}, F_{me}, F_{si} are the calculated fractions of Irminger Water, meteoric and sea ice melt

297 respectively (Irminger Water being the chosen ocean endmember), which sum to 1 by

298 definition. The result is clearly dependent on the exact choice of endmembers for salinity

299 (S_{ir}, S_{me}, S_{si}) and $\delta^{18}O$ (δ_{ir}, δ_{me}, δ_{si}) for the Irminger Water, meteoric and sea ice melt

300 respectively. S_{ms} and δ_{ms} are the measured salinity and $\delta^{18}O$ of each sample.

301 Properties for the sea ice melt and meteoric endmembers (Table 1) were based on values

302 reported in Dodd, Heywood, Meredith, Naveira-Garabato, Marca et al. (2009); Melling and

303 Moore (1995); Meredith et al. (2001); and the CTD observations from the DY081 research

304 cruise. Note that negative sea ice melt percentages reflect a net sea ice formation from the
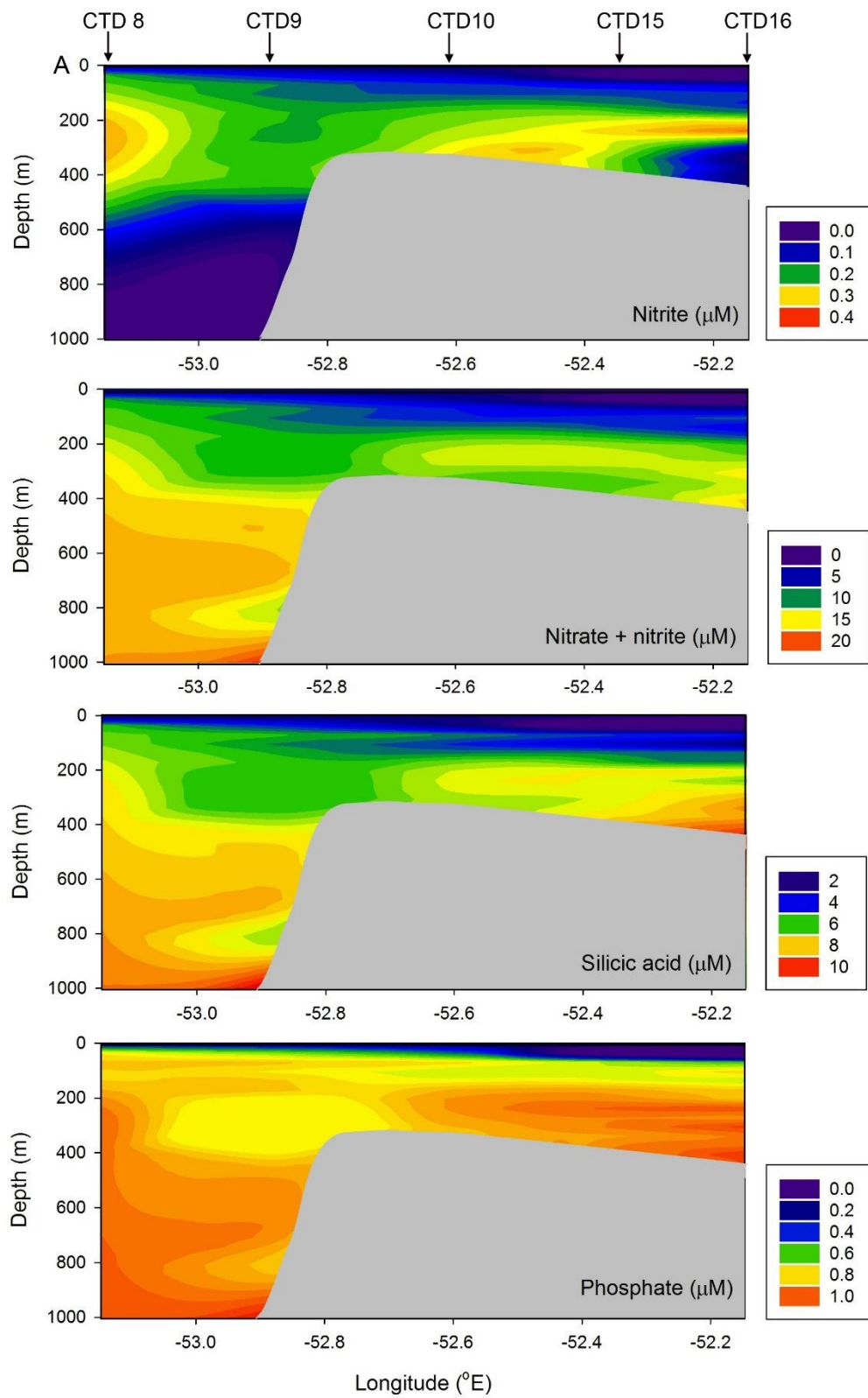
305 water parcel sampled.

306

307 **3. Results**

308

309 EM-122 multibeam swath bathymetry datasets (e.g. Figure 2) are now published on

310 PANGAEA (doi: 10.1594/PANGAEA.892825). The full water column data from CTD profiles

311 and bottles (hydrography, oxygen isotopes, carbonate chemistry, macronutrients e.g. Figure

312 3) are published on PANGAEA (doi.pangaea.de/10.1594/PANGAEA.896544). Here we

313 present a subset of the results, focusing on characterisation of the silica cycle in the water

314 column and sediments.

315

316 **3.1. Silica cycling parameters in the water column and sediments**

317

318 *3.1.1. Water column macronutrients and pigments*

319 The nearshore macronutrient concentrations were typically low (< 11 μM nitrate, < 0.2

320 μM nitrite, < 0.75 μM phosphate and < 5 μM DSi in the upper 50 m of the water column)

321 reaching minima in the surface waters with lowest salinity and lowest $\delta^{18}O$ (an example of

322 which is given in Figure 3a, see also Appendix C). Sections of CTD macronutrient and

323 pigment bottle data from the Nuuk grid, integrated over the top 50m, reveal consistent

324 onshore-offshore trends (an example of which is given in Figure 3b, see also Appendix B).

325 Integrated macronutrient concentrations decreased towards shore concurrent with an
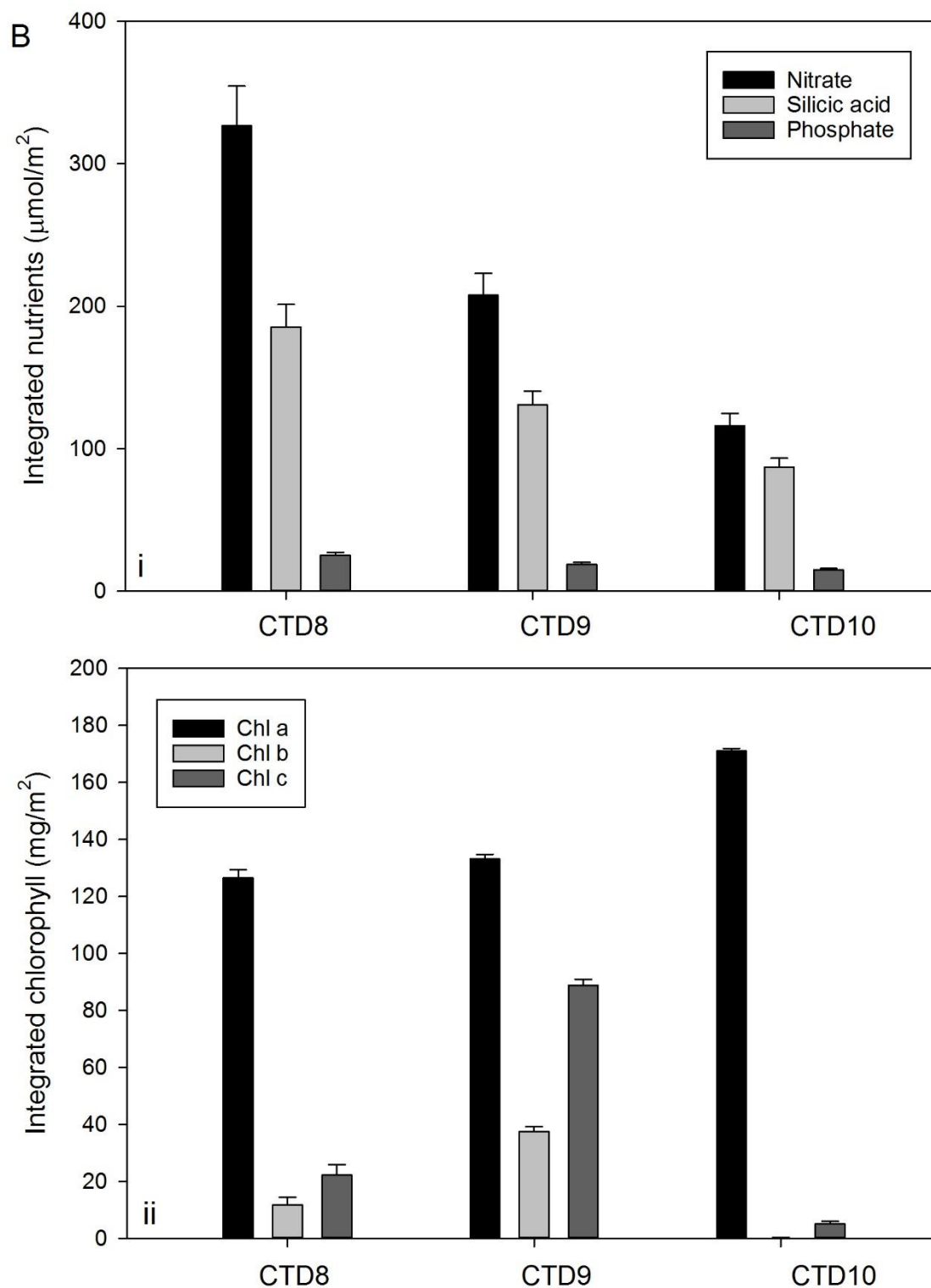
Figure 3: A) Example cross section of macronutrient concentrations from the Nuuk grid (from CTD 8 to CTD 16), showing (from top to bottom): nitrite, nitrate, silicic acid, and phosphate (all in μM). This section crosses the shelf break and occupied the prominent glacial trough, as shown in Figure 2.

B) Example cross section of integrated (top 50 m) macronutrient and algal pigment concentrations from the Nuuk grid (from CTD 8 to CTD 10, see Figure 2). i) Integrated macronutrients; ii) Integrated pigment concentrations. Error bars show propagated errors on integration calculation (±1SD).

326   increase in Si:N. Integrated Chl *a* increased towards shore, indicative that at least some of

327   the macronutrient decrease is a result of biological uptake into biomass. However, the ratio

328   of Chl *a*:Chl *c* peaked at the shelf break, and then decreased again towards shore, indicating

329   a lower diatom proportional contribution to biomass in the same locations as the lowest

330   integrated water column DSi (Figure 3b, see also Appendix C).

331

332   *3.1.2. Diatom productivity*

333   Surface $bSiO_2$ production among the three sampling regions ranged from 0.05 – 0.31

334   µmol Si L^{-1} d^{-1} (Figure 4). For the most part, rates declined with depth; however, the Orphan

335   Knoll site had subsurface maxima at the 20% isolume (~10-20 m) and base of the euphotic

336   zone (i.e. 1% isolume, 20-50 m). The production rates of $bSiO_2$ among the Nuuk profiles

337   were typically higher than Orphan Knoll and Southern Greenland (Figure 4); however,

338   samples incubated in the dark (collected from below the euphotic zone) in Nuuk still had
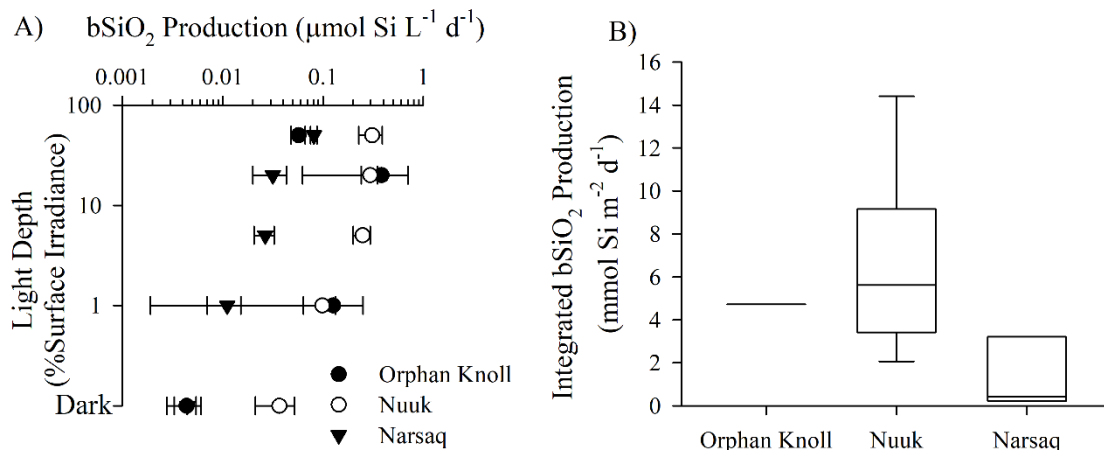
339   measurable production.

Figure 4: Biogenic silica ($bSiO_2$) production during ICYLAB. A) Averaged (±1SD) gross rates of $bSiO_2$ production (µmol Si L^{-1} d^{-1}) versus relative light depth (i.e. 100% is surface, 1% is base of the euphotic zone) among profiles within Orphan Knoll (filled circles), Nuuk (open circles), and Narsaq (filled triangles). B) Box plots of euphotic-zone integrated $bSiO_2$ production (mmol Si m^{-2} d^{-1}) for profiles in Orphan Knoll (n = 2), Nuuk (n = 9), and Narsaq (n = 6).

340

341

342   *3.1.3. Sediment dissolved silicon profiles*

343   Pore water DSi collected from the mega cores and the ROV push cores from the

344   Labrador Sea and coastal Greenland during DY081 expedition range from 49–616 µM (Figure

345   5). All cores generally show an initial increase in pore water DSi with core depth, indicating

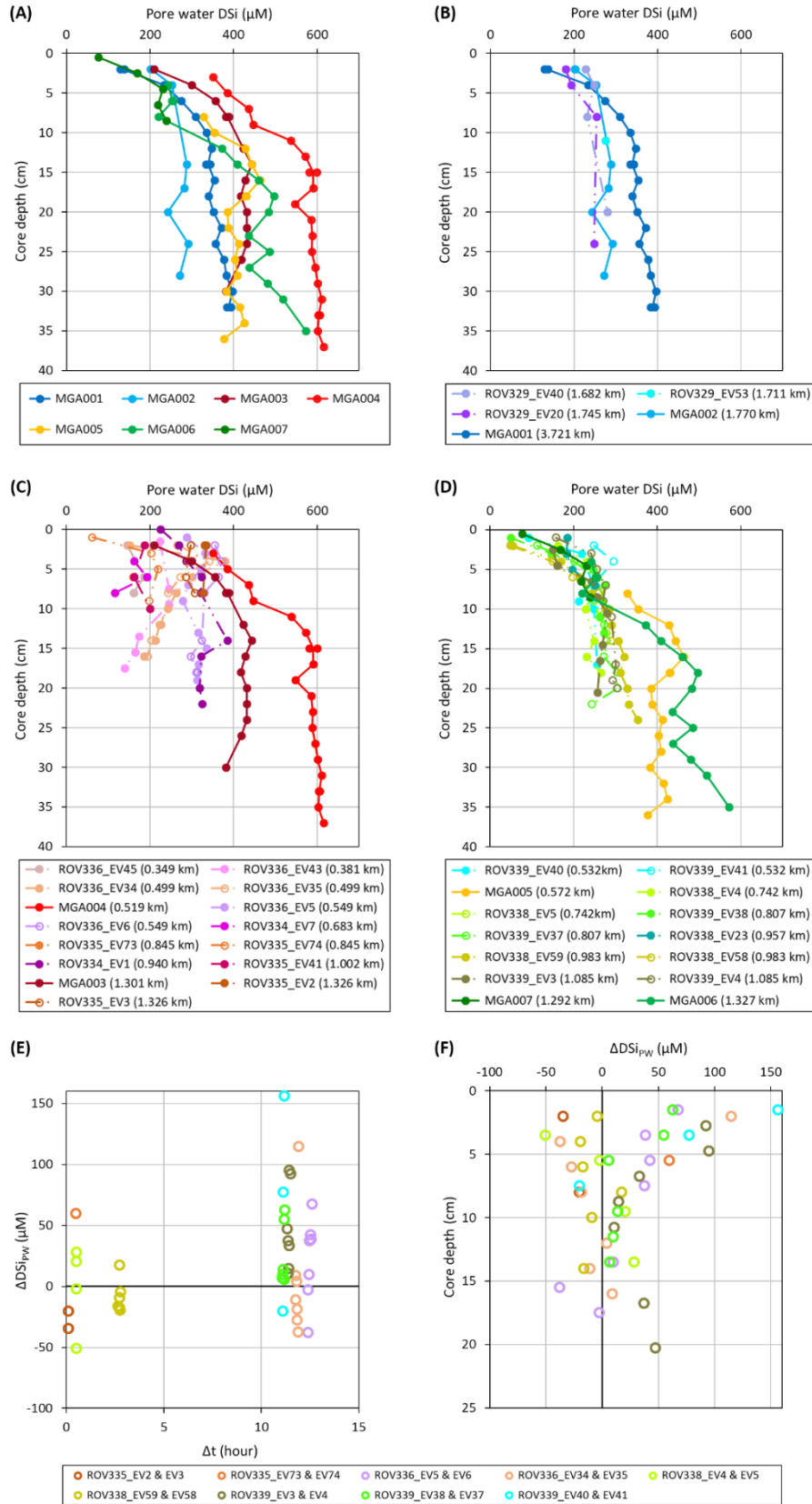*Figure 5: Pore water dissolved silicon concentration (DSi) measurements versus mega core (MGA, solid lines) or ROV push core (dash-dot lines) depths. Results from (a) mega cores, (b) Orphan Knoll cores, (c) cores off Nuuk, and (d) cores off Narsaq and Cape Farewell. Empty circles are results from replicate push cores retrieved at certain sites. Bracketed numbers in plot legends indicate water depths of the sediment cores.*

Differences in pore water dissolved silicon concentration between replicate push cores that were sampled at different time periods (ΔDSiPW). ΔDSiPW was calculated by subtracting push core pore water DSi sampled at the latter time period from the corresponding replicate push core pore water DSi sampled at the earlier time period. The calculation was carried out between measurements from the same or nearby (≤ ±1 cm) sediment core depths. (e) ΔDSiPW versus the time difference between the sampling periods of the replicate cores (Δt), (f) ΔDSiPW versus core depth.

346   supply of Si to bottom waters from the sediment via dissolution. At greater depths, the rates

347   of increase of pore water DSi with depth slow down or even reverses (Figure 5).

348   There is good agreement between pore water DSi results (Figure 5) observed in ROV push

349   cores and mega cores from Orphan Knoll and South Greenland (off Narsaq and Cape

350   Farewell). To the best of our knowledge, this is the first formal comparison of pore water

351   DSi profiling using ROV push cores compared to megacorers, and our results provide

352   confidence to the application of this sampling methodology in future studies, especially in

353   settings where the use of a megacorer proves to be challenging (e.g. complex bathymetry,

354   presence of coarse ice-rafted material). In contrast, there is larger variation in pore water

355   DSi (Figure 5) among the sites off Nuuk (Appendix C), which could in part be related to the

356   greater variability in sediment composition (e.g. ice-rafted debris, fossil fragments) and

357   characteristics (e.g. grain size) observed at these sites. More importantly, the highest pore

358   water DSi concentrations are observed (Figure 5) at the shallowest coastal site closest to

359   Nuuk (Appendix C), which is under the influence of meltwater from glacial fjords.

360   Replicate ROV push cores were collected at certain sites to evaluate any consistent

361   change in pore water DSi with time when the sediment cores were left standing onboard at

362   ambient temperature. Results show only minor discrepancies in pore water DSi: up to ±60

363   μM when the sampling was carried out on paired replicate cores within 3 hours of each

364   other (Figure 5); this is likely due to spatial heterogeneity in sediments and pore waters. In

365   contrast, when pore water sampling was carried out on paired replicate cores more than 10

366   hours apart from each other, there are greater discrepancies with higher DSi values

367   measured in the pore water sampled later in time (Figure 5). Our results suggest that pore

368   water in the upper core depths might not reflect original DSi values if the sampling is carried

369   out more than 10 hours after retrieval of the sediment core.

370

371

4. Discussion

Our multi-disciplinary framework allows a nuanced understanding of the whole silica cycle in this climatically critical region, and specifically, the impact of glacial meltwater in shelf seas and into the open ocean. We are able to address questions surrounding the amount of meltwater reaching the ocean, the mechanism by which it does so, and identify mechanisms for how the meltwater is entrained in coastal and boundary currents. For the main context of this study, we can then use this information to understand better the implications of meltwater inputs on macronutrient distributions and biological production, in particular the supply and uptake of DSi. Lastly, we use our palaeoclimate archives to interrogate past changes in meltwater supplies, which are likely to have had a major impact on nutrient cycling.

4.1.   Bathymetric features and their role in shelf-water dynamics

The shipboard bathymetric and backscatter data provided a rapid insight into the geomorphology of the study regions. The bathymetry features, resulting from their glacial history, are likely to be an important influence on modern shelf-water dynamics and biogeochemical cycling. The bathymetric grids obtained off the W Greenland coast include the dedicated surveys offshore Nuuk, Narsaq and Cape Farewell, in addition to data collected along the transits (Figure 6). They illustrate a wealth of geomorphological features typical of glaciated margins, such as cross-shelf troughs, iceberg ploughmarks, gully systems, submarine canyons and submarine landslides (Dowdeswell, Canals, Jakobsson, Todd, Dowdeswell et al., 2016). Most notably off Nuuk, the inshore-deepening Gothåb (Nuuk) Trough, previously described by Ryan, Dowdeswell and Hogan (2016), is likely to be important in driving instabilities in localised circulation, influencing the mixing of melt and glacially derived material into the shelf waters. The trough harbours a number of drumlins, elongated features typical of glacial weathering, in addition to intricate patterns of iceberg ploughmarks at the shallow trough mouth (Figure 6). Systems of gullies and submarine canyons can be found at both the Gothåb and Narsaq trough-mouth fans, and along the shelf edge (Figure 6). Some of the canyons are cut up to 350 m into the continental slope, and feature steep to near-vertical walls along their flanks together with scoured channels at their floors. Offshore Narsaq, some of the submarine canyons appear to have evolved as a result of retrogressive failures cutting upslope along gullies (Figure 6).
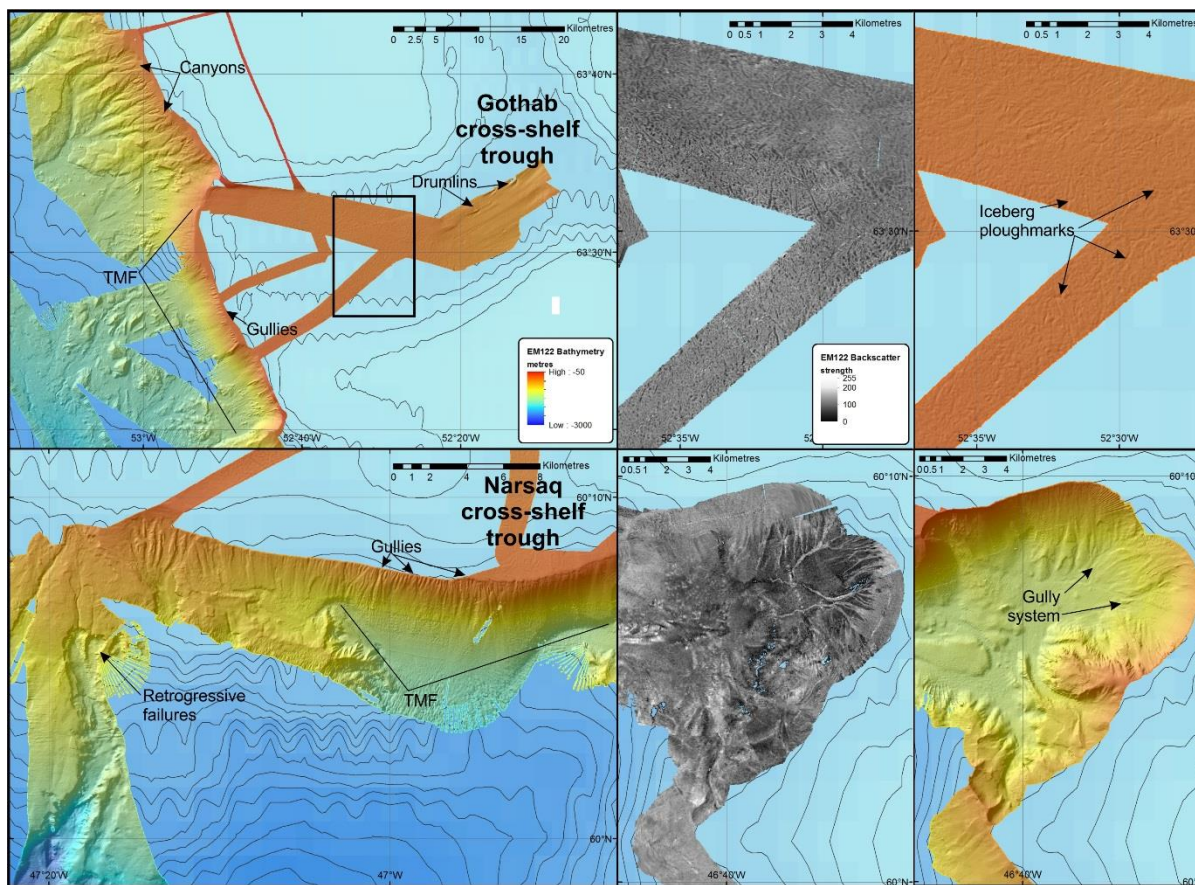
18

Figure 6: Examples of submarine glacial landforms offshore W Greenland identified in the shipboard multibeam data. Background: bathymetry from ETOPO5 (www.ngdc.noaa.gov/mgg/global/etopo5.HTML), contour interval 100 m. Location of maps indicated on Fig. 1. TMF: trough-mouth fan.

405

406

4.2.　　　Physical tracers of glacial meltwater inputs, mixing and advection

407

408　　　　We can use the gridded hydrographic and geostrophic velocity fields to constrain the

409　flow of water across the shelf break, focusing on the Gothåb (Nuuk) Trough CTD section

410　(Figure 2b). The subsurface temperature minimum indicates the core of Polar Surface

411　Water, whilst the subsurface temperature maximum is Irminger Water. The Irminger Water

412　is present between 200 m and 700 m over the continental slope, with a core temperature of

413　4.9°C. There are clear traces of this water mass in the trough also, where warm ($\theta > 4°C$) and

414　saline (S > 34.7) water is observed near the bottom at CTD16 and CTD10. The Polar Surface

415　Water core is spread across the whole section at 50-150 m, with minimum temperatures

416　recorded at the station furthest onshore (CTD16).

417 Geostrophic velocities were calculated by referencing the geostrophic shear to the

418 velocity field measured directly with a Lowered Acoustic Doppler Current Profiler (LADCP).

419 The LADCP velocity field was de-tided, by subtracting the barotropic tide solution obtained

420 from the Oregon State University (OSU) model (Egbert & Erofeeva, 2002). The resultant

421 geostrophic velocity field reveals two surface intensified current cores, one on each side of

422 the trough mouth (Figure 7). The offshore core is associated with a hydrographic front

423 around 15 km west of the shelf break and extends down beyond 400m depth. Its offshore

424 location is consistent with the long-term average position of the West Greenland Current

425 (Myers, Donnelly & Ribergaard, 2009).

426 The inshore velocity core has a less distinct hydrographic signature and therefore its

427 origin is more uncertain at present. One possibility is that the velocity maximum is the result

428 of topographic steering of the inshore portion of the West Greenland Current by the

429 bathymetric trough. Alternatively, it could represent an eddy of offshore water that has

430 detached from the boundary current. A velocity maximum was also detected in a

431 bathymetric trough inshore of Fylla Bank (near Nuuk) in a numerical model simulation

432 (Myers et al., 2009), but there has been no further study into the nature of this feature to

433 date. Such strong inshore current anomalies have significant consequences for the transport

434 of terrestrially-derived freshwater and nutrients.

435 In addition to the mean flows, eddies formed from the West Greenland Current

436 transport water from the boundary current to the interior Labrador Sea, where they

437 contribute to the process of Labrador Sea Water formation (Katsman, Spall & Pickart, 2004).

438 Baroclinic instability is thought to be a key formation mechanism, and years of enhanced

439 baroclinicity tend to coincide with high eddy activity (Rykova, Straneo & Bower, 2015),

440 which transfer hydrographic anomalies into the interior. There is significant baroclinicity in

441 both branches of the WGC in our section, implying that eddy generation may be significant.

442 In addition, wind driven Ekman transport is likely to be a key driver in the export of shelf

443 water across the WGC and into the Labrador Sea interior (Schulze & Frajka-Williams, 2018).

444 Cuny, Rhines, Niiler and Bacon (2002) have suggested that, around this location, the

445 West Greenland Current splits into westward and northward flowing components. However,

446 the location of the splitting, and the partitioning of the water masses involved is not well

447 understood. There are two westward components that flow around the northern perimeter

448 of the Labrador Sea and a northward branch that extends close to the Greenland shelf break

449   (Cuny et al., 2002). Hydrographic signatures of the West Greenland Current have been

450   reported near Greenland to the north, in the vicinity of Davis Strait and Baffin Bay (Cuny,

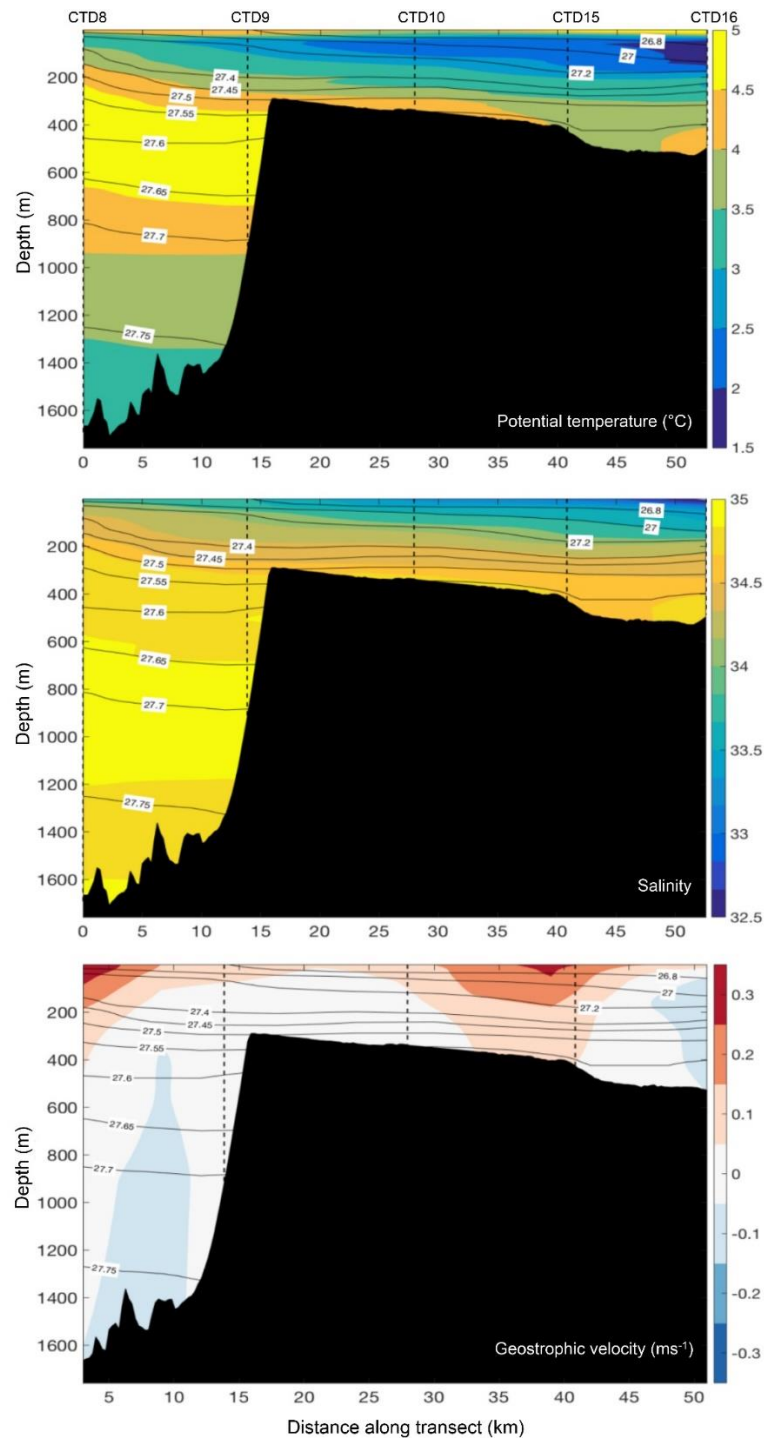451   Rhines & Kwok, 2005; Myers et al., 2009).

452

Figure 7: Gridded vertical sections, from top to bottom, of potential temperature (°C), salinity, and geostrophic velocity (m s⁻¹) along Gothåb (Nuuk) Trough. The direction of geostrophic flow is perpendicular to the CTD section (positive northward and negative southward). The black lines with the white boxed labels are isopycnals, which are lines of constant potential density (in kg m⁻³). The dashed vertical lines indicate the CTD stations, labelled at the top of each panel, from which these vertical sections were derived.

453

4.3. Chemical tracers of glacial inputs

4.3.1. Chemical tracers of meltwater

455

456 Vertical sections of sea ice melt and meteoric percentages based on seawater salinity

457 and δ^{18}O for the Gothåb (Nuuk) Trough CTD section (Figure 8), reveals a negative offshore

458 gradient in both sea ice melt and meteoric water percentages. Higher freshwater

459 concentrations are found in the trough at all depths, highlighting the potential for glacially-

460 sourced waters to reach the outer shelf and the strong boundary currents.

461 Freshwater mass balance calculations have, alternatively, been carried out in the High

462 Arctic using salinity and alkalinity endmembers resulting in robust meteoric water

463 percentage reconstructions (e.g. Hendry et al., 2018; Jones, Anderson, Jutterström & Swift,

464 2008). We compared the two mass balance methods using DY081 data, using both a high

465 meteoric water alkalinity endmember typical of the riverine input to the Arctic Ocean (Jones

466 et al., 2008), and a lower   meteoric water alkalinity endmember typical of glacial meltwater

467 (Meire, Søgaard, Mortensen, Meysman, Soetaert et al., 2015). Our comparison indicates

468 that – irrespective of the endmember values chosen - alkalinity-derived values of meteoric

469 water percentages are impacted by subsurface processes that show correlations with nitrite

470 concentrations and temperature (Appendix C). Such non-conservative behaviour likely arises

471 as a result of enhanced alkalinity flux due to water column nitrification, and/or sedimentary

472 denitrification (Fennel, Wilkin, Previdi & Najjar, 2008; Wolf-Gladrow, Zeebe, Klaas,

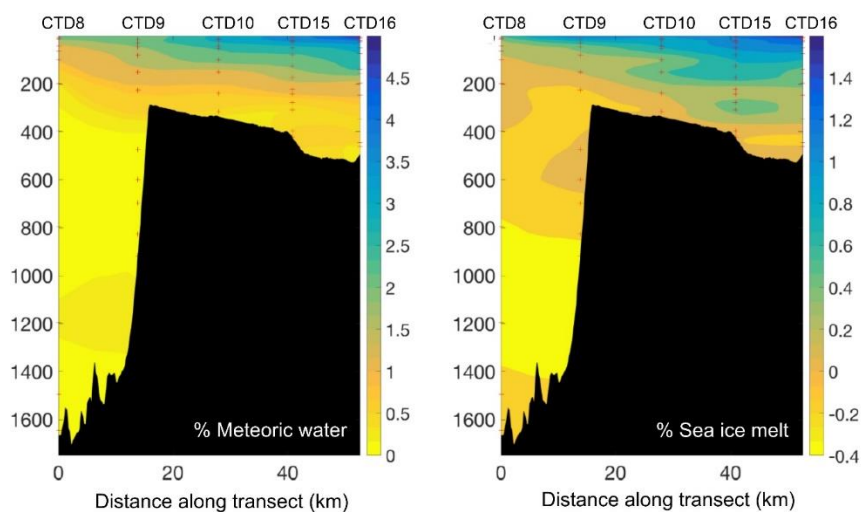473 Körtzinger & Dickson, 2007).

Figure 8: Vertical sections of meteoric water and sea ice melt percentages along Gothåb (Nuuk) Trough. The black area is the bathymetry of the section, as measured by the ship multibeam. Red pluses indicate the bottle sampling locations, with the CTD stations annotated above.

474

475

476   *4.3.2. Geochemical tracers of particulate flux*

477   Radium (Ra) is produced continuously from lithogenic material by the decay of thorium

478   (Th) and thus displays elevated concentrations near any sediment-water interface. Short-

479   lived Ra activities did not show a clear relationship with salinity (Figure 9), but did exhibit

480   informative regional variability. The relatively low activities around Cape Farewell indicate a

481   lack of recent lithogenic input upstream of this region (along the eastern coast of

482   Greenland). From Cape Farewell $^{224}Ra_{XS}$ increases westwards to ~51° W, consistent with

483   increasing cumulative sedimentary inputs into the Greenland coastal current (Figure 9C). As

Figure 9: Spatial distribution of salinity (A), $^{223}Ra_{XS}$ (B) $^{224}Ra_{XS}$ (C) and ^{228}Th (D) from towfish samples taken at 2-5 m depth. Elongated symbols show underway samples which took ~1h to collect. For B-D, inset plots show the same isotope versus salinity in surface waters. Vertical error bars denote ±1 standard error for activities, and horizontal error bars show the standard deviation of salinity measurements taken each minute during the ~1 h sampling interval.

23

484   CTD profiles show that the shallow surface mixed layer sampled by our towfish extended to

485   only 10-20 m, the most likely sources for $^{224}Ra_{XS}$ are glacial meltwater, very shallow

486   sediments within fjords, or resuspended shelf sediments by storm-driven mixing. This signal

487   then decreases towards Nuuk, which will reflect both dilution due to mixing and decay of

488   the short-lived isotope (half-life 3.66 d), and also suggests minimal further lithogenic input

489   into the surface mixed layer. The difference in activity from ~ 9 dpm m^{-3} at ~51° W to < 4.5

490   dpm m^{-3} at the Nuuk sampling stations suggests a decay time of one half-life between these

491   sampling regions, a distance of 300-400 km, although dilution or additional inputs would

492   also affect the measured activity and cannot be fully quantified at present. However, the

493   maximum $^{224}Ra_{XS}$ activities of 8-9 dpm m^{-3} above deep water off the shelf break

494   demonstrate that this lithogenic signal is persistent, with the potential to rapidly transport

495   other glacial and sedimentary-derived compounds far offshore.

496   Although this spatial pattern is not clear in the longer-lived $^{223}Ra_{XS}$ (Figure 9B), the lower

497   overall activity of this isotope - as well as lower detection efficiency - lead to lower signal to

498   noise ratios. It is also likely that regional lithologies may lead to different input patterns due

499   to differing distribution of the ^{227}Ac and ^{228}Th parents.

500   Our analysis also quantifies ^{228}Th, the parent of ^{224}Ra. Due to its lithogenic origin and

501   higher particle reactivity, trends in ^{228}Th may be more closely associated with particulate

502   phases than Ra, especially in our unfiltered samples. Samples collected on fibre are

503   generally assumed to retain the majority of both particulate and dissolved Th, although in

504   coastal waters this approach may underestimate total ^{228}Th where particles can be flushed

505   through the sample, and the activities presented here also include supported activity from

506   ^{228}Ra (the parent of ^{228}Th) within the water column. Nevertheless, our ^{228}Th data (Figure 9D)

507   shows a statistically significant correlation with salinity. We therefore suggest that

508   contrasting patterns in the $^{224}Ra_{XS}$ daughter may be attributed to additional inputs from

509   fjord or shallow shelf sediments, as these inputs are more significant for dissolved species.

510   Additional samples from inner fjord locations and depths below the mixed layer will enable

511   us to differentiate between inputs from marine and glacial sediments.

512

513   **4.4. Diatom productivity in glacially-influenced shelf seas**

514   Despite the low nutrient concentrations, bSiO$_2$ production rates were significant in the

515   meltwater influenced waters off the shelf and slope. Similar surface DSi concentrations are

516   observed in the open-ocean gyres (e.g. North Pacific, Brzezinski, Krause, Church, Karl, Li et

517   al. (2011); North Atlantic, Krause, Nelson and Lomas (2010)) and typically do not support

518   high rates of diatom productivity. Spring-season $bSiO_2$ production rates in Svalbard and the

519   Barents Sea (Krause, Duarte, Marquez, Assmy, Fernández-Méndez et al., 2018) and at the

520   MarineBasis Nuuk station in Godthaabsfjord (Krause, Schulz, Rowe, Dobbins, Winding et al.,

521   In review) were routinely lower than those quantified at Orphan Knoll or Nuuk. The active

522   production below the euphotic zone suggests either recently exported diatoms (e.g. from

523   surface waters within 1-2 days) or the presence of siliceous and active Rhizaria (Biard,

524   Krause, Stukel & Ohman, 2018; Biard, Stemmann, Picheral, Mayot, Vandromme et al., 2016).

525   Integrated $bSiO_2$ production rates in the euphotic zone ranged two orders of magnitude,

526   0.13 – 14.4 mmol Si m^{-2} d^{-1}. Four of the six stations off Southern Greenland had integrated

527   rates <1 mmol Si m^{-2} d^{-1}, similar to mid-ocean gyres (Brzezinski et al., 2011), whereas all

528   other profiles during the cruise exceeded 2 mmol Si m^{-2} d^{-1}. These rates are on the lower

529   end for the Southern Ocean (1-93 mmol Si m^{-2} d^{-1}, Nelson, Treguer, Brzezinski, Leynaert and

530   Queguiner (1995)) but are similar to Svalbard and the Barents Sea during spring (0.3–1.5

531   mmol Si m^{-2} d^{-1}, Krause et al. 2018). Overall, diatom $bSiO_2$ production consumed 4%

532   (median) – 10% (average) of the euphotic zone DSi inventory daily. These data are the first

533   such reports for this region of the Labrador Sea and Greenland, and demonstrate a

534   surprisingly active diatom assemblage despite low nutrients, temperature, and biomass.

535

536   **4.5. Influence of glacial meltwaters in the open ocean: Si cycling as a case study**

537   Although glacial meltwaters exhibit elevated concentrations of some dissolved nutrients

538   and reactive phases (e.g. Hawkings et al., 2017), glacial fjords – the conduits between the

539   source of these nutrients and the open ocean – are characterised by complex physical,

540   chemical and biological processes and are highly variable in space and time (Hopwood,

541   Carroll, Browning, Meire, Mortensen et al., 2018). Despite the highly heterogeneous nature

542   of these environments, we can use the findings from DY081 to shed more light on the key

543   common processes that characterise the transfer of nutrients across the land-ocean

544   interface, which will likely vary in rates and importance between different glaciated regions.

545   In many high-latitude regions, upwelled waters are thought to dominate the supply of

546   nutrients to the euphotic zone supporting most of the primary production. For example, off

547   the West Antarctic Peninsula (WAP), biological "hotspots" were thought to be fed by

548   upwelling Circumpolar Deep Water (CDW) being channelled onto the shelf via glacially

549   carved canyons (Schofield, Ducklow, Bernard, Doney, Patterson-Fraser et al., 2013).

550   However, there is increasing evidence that CDW is heavily modified as it transits onto the

551   shelf likely due to a flux of silica and iron from shallow marine sediments (Henley et al.,

552   2018; Sherrell et al., 2018). However, even in these relatively nutrient-rich environments,

553   there is still some important direct input from glacial meltwaters (e.g. Annett, Skiba, Henley,

554   Venables, Meredith et al., 2015) due to the release of reactive phases and promotion of

555   biological mediation of nutrient cycling through the formation of organic matter and

556   biogenic minerals.

557   Despite different boundary conditions compared to the WAP, similar processes are likely

558   to be happening in glaciated regions of SW Greenland. For example, elevated DSi (>20 μM)

559   in Greenlandic fjords measured in surface waters (Hawkings et al., 2017) cannot simply be

560   explained by mixing between the freshwater and marine end-members: these

561   concentrations are higher than the freshwater endmember, and there are no seawater

562   masses with sufficiently high DSi concentrations in the top 100m to supply this flux (Figure

563   3, see also Appendix C). The fjord water must be modified – in an analogous way to the WAP

564   – likely by particle-water interactions, including the release of DSi from reactive phases

565   derived from glacial weathering products, or biogenic silica (Hawkings et al., 2018; Hawkings

566   et al., 2017; Meire et al., 2016). This modification may be active in the water column, as well

567   as at the sediment-water interface, in the fjords as well as in the shallow water shelf-

568   sediments (Figure 5).

569   However, despite this enrichment within the fjord, the low-salinity waters reaching the

570   coastal ocean are low in DSi as a result of uptake mechanisms that are active as the fjordic

571   waters reach the shelf; our forthcoming studies of uptake kinetics and algal physiology from

572   within the fjords themselves will elucidate whether biological uptake is playing a key role in

573   Si cycling in these regions. Although there is apparently a limited supply of DSi exported

574   from fjords, there appears to be active cycling of silica by diatoms in coastal waters. Our

575   findings show the potential for meteoric waters, and glacially-derived particles, to be

576   exported as far as the coastal and boundary currents, and into the open ocean, where

577   further processing could act to release bioavailable elements. Whilst some of these

578   exported particles may dissolve within the water column during sinking, some will reach the

579   sediment-water interface. Pore water DSi can be used to evaluate the chemical changes of

580   the sediments post-deposition such as the dissolution of this reactive glacial material in

581   addition to dissolution of biogenic silica remains of diatoms and sponges, secondary or

582   'reverse' weathering, and the recycling of DSi back to the bottom waters (Rahman, Aller &

583   Cochran, 2017). The high, but variable, DSi concentrations found in the pore waters at our

584   coastal study sites point towards high rates of benthic regeneration fluxes. Calculated

585   sedimentary diffusive fluxes off SW Greenland, using the approach of Ragueneau, Gallinari,

586   Corrin, Grandel, Hall et al. (2001), range from 0.1-0.3 mmol Si m^{-2} d^{-1}, and are at least 10% of

587   the diatom production rates. Our findings suggest that the total DSi flux across the

588   sediment-water interface, including from advective processes, could rival the magnitude of

589   water column biogenic silica production rates. The high uptake rates of diatoms, together

590   with this rapid recirculation of DSi across the sediment-water interface, points towards a

591   silica cycle maintained by strong pelagic-benthic coupling.

592

593   **4.5. Approaches to reconstructing glacial meltwater inputs through time**

594   Glacial meltwaters are enriched in both dissolved and particulate nutrients, including

595   silicon, and our new data highlight that these meltwaters extend across the shelf into

596   boundary currents. In the context of the marine silicon cycle, our data show that, whilst DSi

597   reaching the shelf waters from the glacial fjords may be low, diatom activity is surprisingly

598   high. DSi must be reaching the surface, potentially by mixing with modified shelf waters. Our

599   Ra isotopic data (section 4.3.2.) reveal that there is input of glacial particles into these shelf

600   waters, potentially via sediment reworking, which may contribute bioavailable silicon via

601   dissolution both in the water column and at the sediment-water interface. This system is

602   likely to be sensitive to glacial inputs, and so quantifying changes in meltwater fluxes

603   through time - using a variety of climate archives - is going to be key to understanding shelf

604   and slope productivity during past episodes of climatic change.

605

606   *4.5.1. Fossil deep-sea corals*

607   The geochemistry of fossil skeletons of deep-sea corals has the potential to record

608   aspect of past environmental conditions (Chen, Robinson, Beasley, Claxton, Andersen et al.,

609   2016; Robinson, Adkins, Frank, Gagnon, Prouty et al., 2014). In particular, water masses

610   distribution and food supply are thought to be important for deep-sea coral populations off

611   the West Greenland margin. Given their environmental sensitivity, cold-water coral

612   distributions are likely to susceptible to changes in water mass properties and primary

613   production caused by meltwater inputs. In 2017, the first living samples of the cold-water

614   scleractinian coral, *Lophelia pertusa*, were collected from approximately 60° 22'N off the

615   Greenland within a layer of relatively warm, modified Atlantic Water (Kenchington,

616   Yashayaev, Tendal & Jørgensbye, 2017).

617   We have now been able to make in situ observations of cold water corals off

618   Greenland, as well as showing that corals have been present on the Greenland Margin for at

619   least 10,000 years (Figure 10). These first populations likely appeared with melting of the

620   large ice fields of the last glacial period. Supporting prior research, we also found that

621   scleractinian corals have been present further south on Orphan Knoll for at least 130,000

622   years (Figure 10; Cao, Fairbanks, Mortlock & Risk, 2007; Hillaire-Marcel, Maccali,

623   Ménabréaz, Ghaleb, Blénet et al., 2017). In both locations our suite of dates show that the

624   populations have not been stable. This observation implies shifts in environmental pressures

625   over these timescales, likely driven by a shift in balance between warmer Atlantic waters

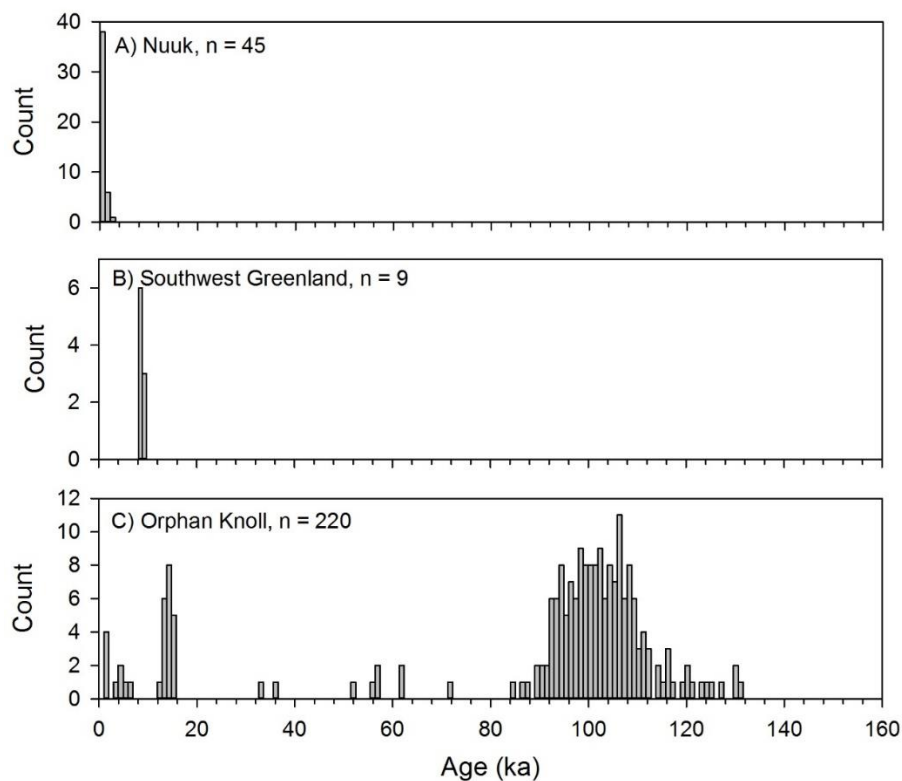626   and cold meltwater-rich polar waters.

Figure 10: Uranium-thorium age data for fossil corals collected during DY081.

627

628   *4.5.2. Marine sediments and past glacial meltwater inputs*

629   During the last ice age, catastrophic iceberg discharge events episodically flooded the

630   subpolar North Atlantic with meltwater (Heinrich, 1988). Evidence suggests that these

631   "Heinrich events" (Broecker, Bond, Klas, Clark & McManus, 1992), were related to, and may

632   have acted as the trigger for (Broecker, 2003; Clark, Pisias, Stocker & Weaver, 2002),

633   dramatic changes in ocean circulation (McManus, Francois, Gherardi, Keigwin & Brown-

634   Leger, 2004) and heat distribution that were felt globally (e.g. Wang, Cheng, Edwards, An,

635   Wu et al., 2001). In addition to global impacts, changes in ice sheet dynamics and meltwater

636   inputs would also have had considerable impacts on more regional biogeochemical cycling.

637   While previous work has identified the existence of eight such events over the last 70 ka

638   (Andrews, Jennings, Kerwin, Kirby, Manley et al., 1995; Bond, Heinrich, Broecker, Labeyrie,

639   McManus et al., 1992; Bond & Lotti, 1995; Rashid, Hesse & Piper, 2003; Stoner, Channell &

640   Hillaire-Marcel, 1996), questions remain about the origin(s) of these events, their trigger(s)

641   and the nature of their primary signatures across the North Atlantic (Andrews & Voelker,

642   2018). Gravity cores collected at Orphan Knoll (DY081-GVY002 & GVY002), Southwest

643   Greenland (DY081-GVY003) and Cape Farewell (DY081-GVY004 & GVY 005) represent new

644   opportunities to constrain the timing, geometry and character of iceberg discharge and

645   glacial meltwater release in the paleo record.

646   Existing work on marine sediment cores from the high latitude North Atlantic has

647   employed a variety of proxies to identify pulses of meltwater delivery and associated ice

648   rafted debris delivery. Previously applied proxies include $^{230}Th_{xs,0}$ (to assess changes in

649   sedimentary fluxes (McManus, Anderson, Broecker, Fleisher & Higgins, 1998)), counts of IRD

650   and foraminifera (to identify the relative abundance of terrestrially-derived debris and

651   foraminifera (Heinrich, 1988)), foraminifera census (to determine the relative abundance of

652   cold-dwelling planktonic species such as *N. pachyderma s.* (Ruddiman, Sancetta &

653   McIntryre, 1977)), $\delta^{18}O$ of *N. pachyderma s.* (to quantify the cooling and/or freshening of

654   surface waters (Bond, Broecker, Johnsen, McManus, Labeyrie et al., 1993)), magnetic

655   susceptibility (to identify detrital sediment (Grousset, Labeyrie, Sinko, Cremer, Bond et al.,

656   1993)), x-ray diffraction (XRD) (to assess changes in the abundance of quartz and plagioclase

657   feldspar (Moros, Kuijpers, Snowball, Lassen, Bäckström et al., 2002; Moros, McManus,

658   Rasmussen, Kuijpers, Dokken et al., 2004)), and X-ray fluorescence (XRF) (to identify changes

659   in sedimentary elemental ratios (Hodell, Channell, Curtis, Romero & Röhl, 2008)).

660   Unfortunately, the comparison of sediment core records has been limited by difficulties in

661   establishing tightly constrained chronologies. This has impeded analysis of the triggers of

662   events and the range of their influence (Andrews & Voelker, 2018). While previous work has

663   utilized one or more of the proxy approaches identified above, complete assessment of the

664   proxies described above, in a single core, would greatly assist in interpreting the

665   paleoceanographic record. In addition, despite the widespread inference that icebergs

666   originated from the Laurentide ice sheet during these events (Bond & Lotti, 1995; Broecker,

667   2003; Hodell et al., 2008; McManus et al., 1998), relatively fewer detailed studies have

668   examined their imprint and consequences in the proximal Labrador Sea (Andrews &

669   Voelker, 2018).

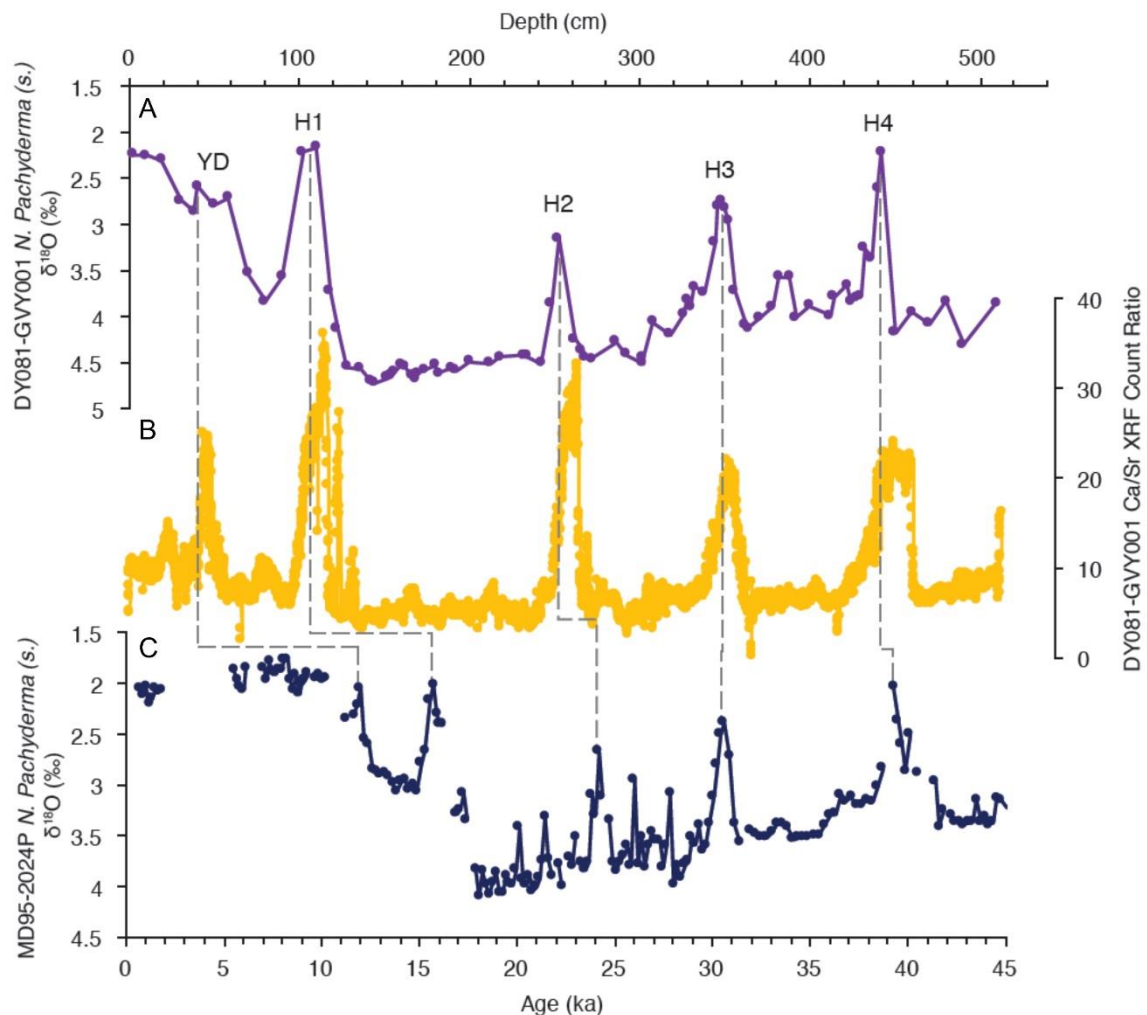*Figure 11: Proxies for North Atlantic Heinrich Events. a) N. Pachyderma (s.) $\delta^{18}O$ from DY081-GVY001 (purple). b) Ca/Sr XRF count ratio from DY081-GVY001 (yellow). c) N. Pachyderma (s.) $\delta^{18}O$ (Hillaire-Marcel & Bilodeau, 2000) on the age model of Lynch-Stieglitz, Schmidt, Henry, Curry, Skinner et al. (2014) (navy blue). Vertical grey dashes suggest age-depth assignments for DY081-GVY001.*

670

671   Our goal in analysing the new DY081 cores is to use a wide range of proxies to address

672 temporal relationships and the spatial signatures of Heinrich events. Our findings show that

673 GVY001 (Orphan Knoll) represents a record of continuous sedimentation from 40-50 ka to

674 present and likely captures the Younger Dryas and Heinrich events 1-4 (Figure 11). In

675 GVY001 Heinrich event signatures have been identified in records of IRD counts, the $\delta^{18}O$ of

676 planktonic foraminifera, XRD and XRF scans. These results confirm the utility of using the

677 suite of proxies in DY081 cores to tie together previously incomparable records from

678 sediment cores in which disparate proxies have been applied, to reconstruct meltwater

679 inputs in the region back through time.

680

681 **5. Synthesis and Outlook**

682   Coastal and shelf sea biogeochemical research in the polar regions requires high-

683 resolution spatial and temporal datasets, due to the inherent heterogeneous nature of the

684 high-latitude margin settings. Whilst obtaining the necessary temporal resolution is

685 challenging, especially in the absence of expensive long-term monitoring programs, it is

686 possible to combine traditional physical and biogeochemical measurements with novel

687 isotopic and observational methods that integrate signals over a variety of timescales (days

688 to thousands of years). Stable and radiometric isotope geochemistry also allows the

689 identification of common processes within this highly-variable system, which are active over

690 given timescales. All of these approaches can be combined with palaeoceanographic

691 techniques to obtain a reliable baseline for pre-industrial conditions, and also look for

692 analogues of future change from the past.

693   In the context of the marine silica cycle, our findings from DY081 are able to show that:

694 • There are strong mean flows that are conducive to eddy generation, which will likely

695   transport freshwater from the margin into the boundary currents that supply the

696   Labrador Sea;

697 • Oxygen isotopes robustly trace meteoric water composition adjacent to Greenland,

698   with near-surface concentrations of 5% over the shelf reflecting significant glacial

699   discharge;

700 • Ra isotopes indicate additions of glacial meltwater and sedimentary particulates are

701   spatially heterogeneous and rapidly transported;

702 • Low macronutrient concentrations (e.g. DSi) are found in coastal waters influenced
703   by glacial melt;

704 • Diatoms are surprisingly active given the low nutrient availability and low
705   temperature (i.e. consuming 5-10% of euphotic zone Si daily);

706 • There is a strong benthic flux of DSi from sediments;

707 • Fossil corals can be used to track changes in benthic ecosystems through time, likely
708   influenced by water mass distribution;

709 • Sediment cores recovered of sufficient length and resolution to reconstruct
710   meltwater inputs at least back to 45 ka (i.e. Heinrich events 0-4).

711

712 **Acknowledgments**

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722

723   Table 1: End-member values used in the mass balance calculations.

	Irminger	Meteoric	Sea ice
Salinity	34.88	0	3
$\delta^{18}O$ (‰)	+0.34	c. −21	Surface values +2.1

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725

APPENDIX A: Oceanographic setting

The strong West Greenland Current (WGC) brings cold Arctic Water (AW) around the southern tip of Greenland and northwards into the Labrador Sea (Yang et al., 2016). The Irminger Current (IC) brings in warmer North Atlantic Water (NAW) from the North Atlantic into the Labrador Sea – this water is ultimately derived from the Gulf Stream. The typical water column structure near coastal Western Greenland is stratified by salinity, comprising cold, surface water (found shallower than approximately 100 m) that consists of AW and additional meltwater, overlying a strong thermocline; NAW (temperature > 3˚C, salinity < 34.5) is found below the thermocline, with the water temperature peaking at a depth of approximately 400m, most likely representing the core of Irminger Water inflow (McCartney and Talley, 1982).

At approximately 64 °N, the latitude of Nuuk, the WGC bifurcates into the Labrador Current (LC), and a proportion is diverted into the interior of the Labrador Sea, where deep water formation occurs by winter-time convection driven by oceanic heat loss (McCartney, 1992). The newly formed Labrador Sea Water (LSW) enters the North Atlantic as the Deep Western Boundary Current, to form the upper layers of North Atlantic Deep Water (NADW), which subsequently become the intermediate layers of the North Atlantic meridional overturning circulation. By the time the boundary current reaches Orphan Knoll (Figure 2a), sub-thermocline warm, saline waters are underlain by the LSW and overflow waters (likely Gibbs Fracture Zone Water and Demark Strait Overflow Water) (Yang et al., 2016).

APPENDIX B: Details of methodologies

Full details of on-board methodology and approach can be found in the DY081 cruise report (Hendry, 2017), but are summarised briefly here.

B.1. Water column sampling and on-board processing: glacial meltwater inputs, nutrients, and phytoplankton

Water column samples were collected using Niskin bottles attached to the CTD rosette (10L volume) and the Remotely Operated Vehicle (ROV) *Isis* (4 L volume), and via a trace-metal clean towfish.

759   Duplicate samples for inorganic macronutrients were filtered using either an Acropak

760   or in-line polycarbonate filter (0.2 μm) into acid-cleaned and rinsed high density

761   polyethylene (HDPE) bottles and frozen immediately at -20°C. Clean handling techniques

762   were adopted and only Semperguard vinyl non-powdered gloves were used for the sample

763   handling. Samples for biogenic/amorphous silica were filtered through 25mm 0.6 μm

764   polycarbonate filters, dried and stored for analysis back on land.

765   Samples were also collected for water oxygen isotope composition (δ^{18}O) and

766   carbonate chemistry parameters (pH, alkalinity), which are used for investigating freshwater

767   input in high-latitude regions (Hendry et al., 2018; Meredith et al., 2008; Thomas et al.,

768   2011). For δ^{18}O, an unfiltered water sample was sealed tightly in a (rinsed) 60 mL HDPE

769   plastic bottle and stored in a cool, dark storage location. For carbonate chemistry, a 250 mL

770   borosilicate glass bottle was rinsed twice with seawater from the Niskin before being filled

771   using a PVC tube and allowed to overflow one volume; a glass stopper was placed in the

772   bottle neck to displace excess seawater then 2.5 mL of seawater was pipetted off to allow a

773   1% headspace. The sample was poisoned with 50 μL saturated mercuric chloride solution

774   and sealed, homogenised and stored in a cool, dark storage location.

775   Phytoplankton pigments were analysed on board, and compared to sensor-derived

776   fluorescence data, to assess algal standing stocks in relation to meltwater input. Seawater

777   was filtered using GF/F filters and then frozen at -20 °C until extraction. A trichromatic

778   method (Mackereth et al., 1978) was used to determine chlorophyll (Chl) a, b, and c

779   spectrophotometrically in the near surface seawater samples. Chlorophyll extraction was

780   carried out using aqueous acetone buffered with magnesium carbonate, for 24 hours in the

781   dark at 4°C. The samples were then centrifuged and analysed at 750 nm (to correct for

782   turbidity), 664 nm, 647 nm, and 630 nm on a V-1200 Vis spectrophotometer. Absorbance

783   values were then used in equations 1 to 3 to calculate the concentration of Chl *a, b*, and *c*

784   per volume of filtered sample (Eq. 4).

785   Chl *a* (mg/L) = 11.85*(OD664) − 1.54*(OD647) − 0.08*(OD630)   (1)

786   Chl *b* (mg/L) = 21.03*(OD647) − 5.43*(OD664) − 2.66*(OD630)   (2)

787   Chl *c* (mg/L) = 24.52*(OD630) − 7.60*(OD647) − 1.67*(OD664)   (3)

788   Chl *x*, mg/m^3 = (Chl *x*) * extract volume, L/ Volume of sample, m^3 (4)

789

B.2. Additional laboratory techniques

791   Seawater oxygen isotope ($\delta^{18}O$) measurements were made using the CO_2 equilibration

792   method with an Isoprime 100 mass spectrometer plus Aquaprep device at the British

793   Geological Survey (Keyworth). 200µl samples of water were loaded into exetainers (3.7ml

794   Labco Ltd.) and placed in the heated sample tray at 40°C. The exetainers were then

795   evacuated to remove atmosphere, then flushed with CO_2 and left to equilibrate for between

796   12 (first sample) - 37 (last sample) hours. Each individual gas sample was then admitted to

797   the cryogenic water trap where any water vapour was removed. The dry sample gas was

798   then expanded into the dual inlet where it was measured on the transducer before being

799   expanded in the dual inlet bellows. Ionvantage software balanced the reference bellows

800   relative to its volume. The sample and reference CO_2 gases entered alternatively into the

801   Isoprime100 through the dual changeover valve for isotope ratio measurement. In each run

802   two laboratory standards (CA-HI and CA-LO) plus up to two secondary standards were

803   analysed in triplicate. The value of these laboratory standards has been accurately

804   determined by comparison with international calibration and reference materials

805   (VSMOW2, SLAP2 and GISP) and so the $^{18}O/^{16}O$ ratios (versus VSMOW2) of the unknown

806   samples can be calculated and are expressed in delta units, $\delta^{18}O$ (‰, parts per mille).

807   Isotope measurements used internal standards calibrated against the international

808   standards VSMOW2 and VSLAP2. Errors are typically +/− 0.05‰ for $\delta^{18}O$.

809   Carbonate analysis was carried out at GEOMAR, Germany. For Total Dissolved Inorganic

810   Carbon (TDIC), carbonate species were converted to CO_2 by addition of phosphoric acid

811   (10% in 0.7 M NaCl), this generated CO_2 is then carried into the measurement cell using N_2

812   and analysed by coulometric titration using a VINDTA 3C (Marianda, Germany) connected to

813   a 5011 coulometer (UIC, USA). For Total Alkalinity (TA) samples are titrated with 0.1 M HCl

814   (prepared in 0.7 M NaCl) in 150 µL increments until the carbonic acid equivalence point is

815   reached. The titration is monitored with the VINDTA 3C in a closed cell titration (Dickson et

816   al., 2007). Measurements were calibrated using certified reference material from Prof.

817   Dickson, Scripps. The temperature, salinity, and nutrient concentrations of the samples at

818   time of sampling are then combined with the TDIC and TA measurements to calculate CO_2

819   system parameters (pH and pCO_2).

820   Samples for inorganic nutrients were all analysed at the Plymouth Marine Laboratory

821   using the latest GO-SHIP (Hydes et al., 2010) recommended defrosting technique of heating

822   in a warm water bath for 45 minutes from frozen and then equilibrating to room

823   temperature for another 30 minutes before analysis. The analysis was carried out using a

824   SEAL analytical AAIII segmented flow colorimetric auto-analyser using classical analytical

825   techniques for nitrate, nitrite, silicic acid (or DSi) and phosphate, as described in Woodward

826   and Rees (2001). Clean sampling and handling techniques were employed during the

827   defrosting, sampling and manipulations within the laboratory, and where possible carried

828   out according to the International GO-SHIP nutrient manual recommendations of Hydes et

829   al. (2010). Seawater nutrient reference materials (KANSO Ltd. Japan) were also analysed to

830   check analyser performance and to guarantee the quality control of the final reported data.

831   The typical uncertainty of the analytical results were between 2-3%, and the limits of

832   detection for nitrate and phosphate were 0.02 µM, 0.01 µM for nitrite, and silicic acid did

833   not ever approach the limits of detection.

834   We dated 274 fossil scleractinian corals from the three main target sites (Orphan

835   Knoll, Nuuk, South Greenland) using a reconnaissance dating technique based on the decay

836   of uranium to thorium (Spooner et al 2015, Chen et al 2015).

837   Foraminifera samples for stable isotope analysis were processed and analysed at the

838   Lamont-Doherty Earth Observatory of Columbia University. Samples were freeze-dried and

839   then washed through a 63 µm sieve and the >63 µm fraction dried at 45°C overnight. Five to

840   ten specimens of *Neogloboquadrina pachyderma* (sinistral) were picked from the >250 µm

841   size fraction, weighed to ensure consistent sample sizes and then analysed on a Thermo

842   Delta V Plus with Kiel IV individual acid bath device. Values were calibrated to the VPDB

843   isotope scale with NBS-19 and NBS-18. Reproducibility of the in-house standard (1SD) is

844   ±0.06‰ for δ^{18}O and ±0.04‰ δ^{13}C.

845   Ca and Sr intensities (count rates) were measured with an x-ray fluorescence (XRF)

846   core scanner (ITRAX, Cox Ltd., Sweden) at the British Ocean Sediment Core Research Facility

847   (BOSCORF). Split core surfaces were smoothed and covered with polypropylene film to

848   minimize desiccation during analysis. Elemental counts were collected at 1 mm resolution,

849   using an integration time of 2s and a molybdenum x-ray source set to 30kV and 30mA.

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APPENDIX C: Supplementary figures
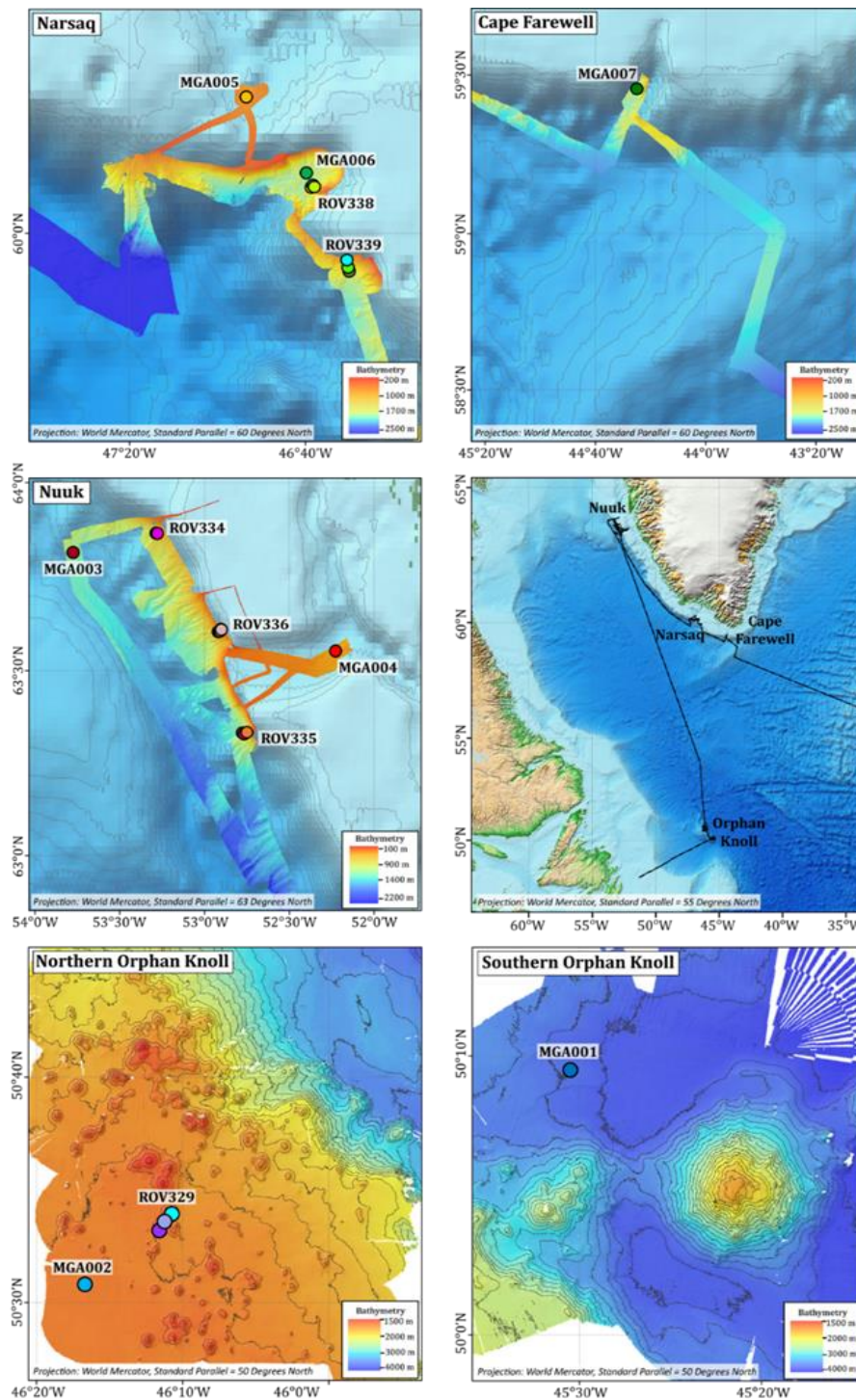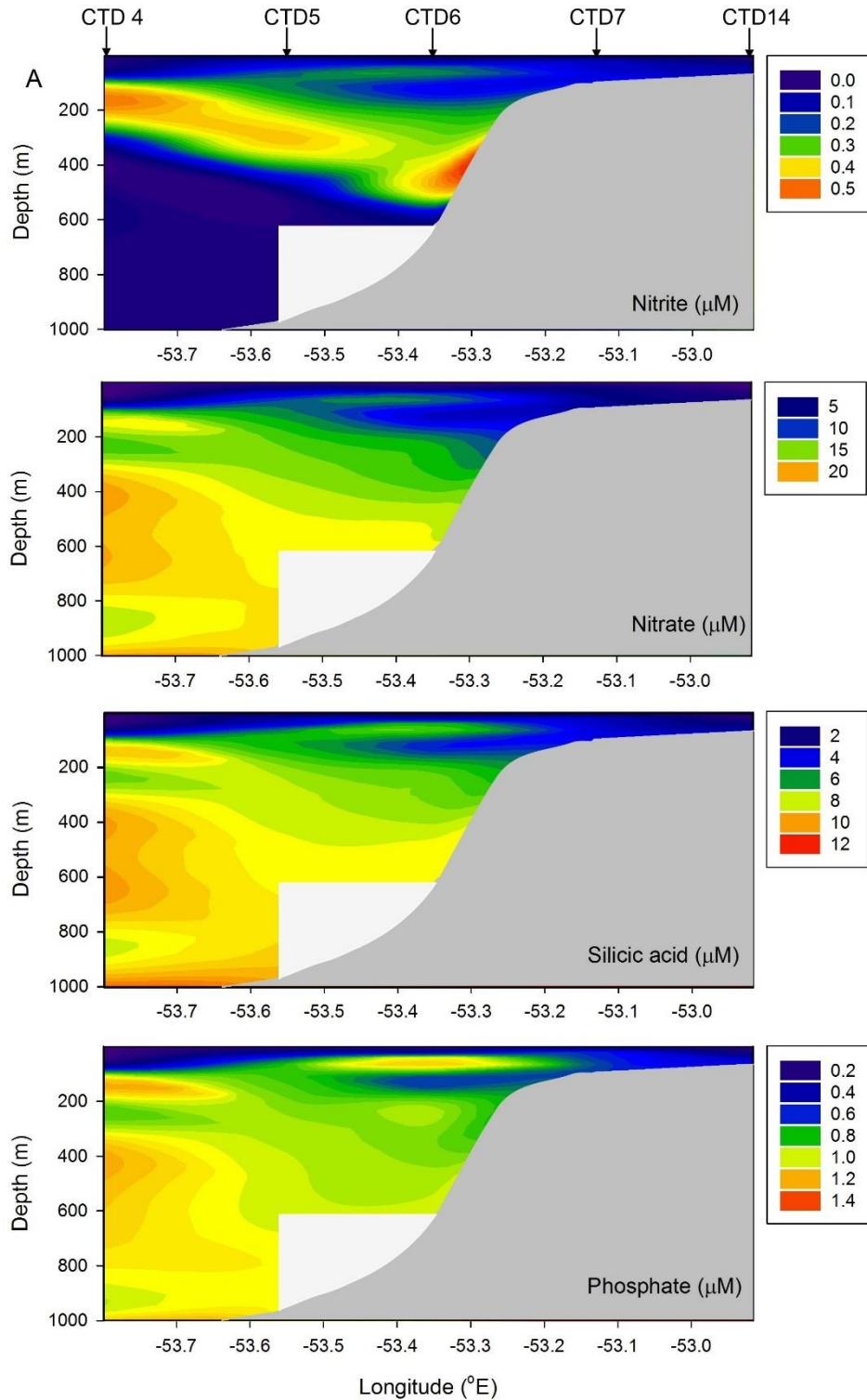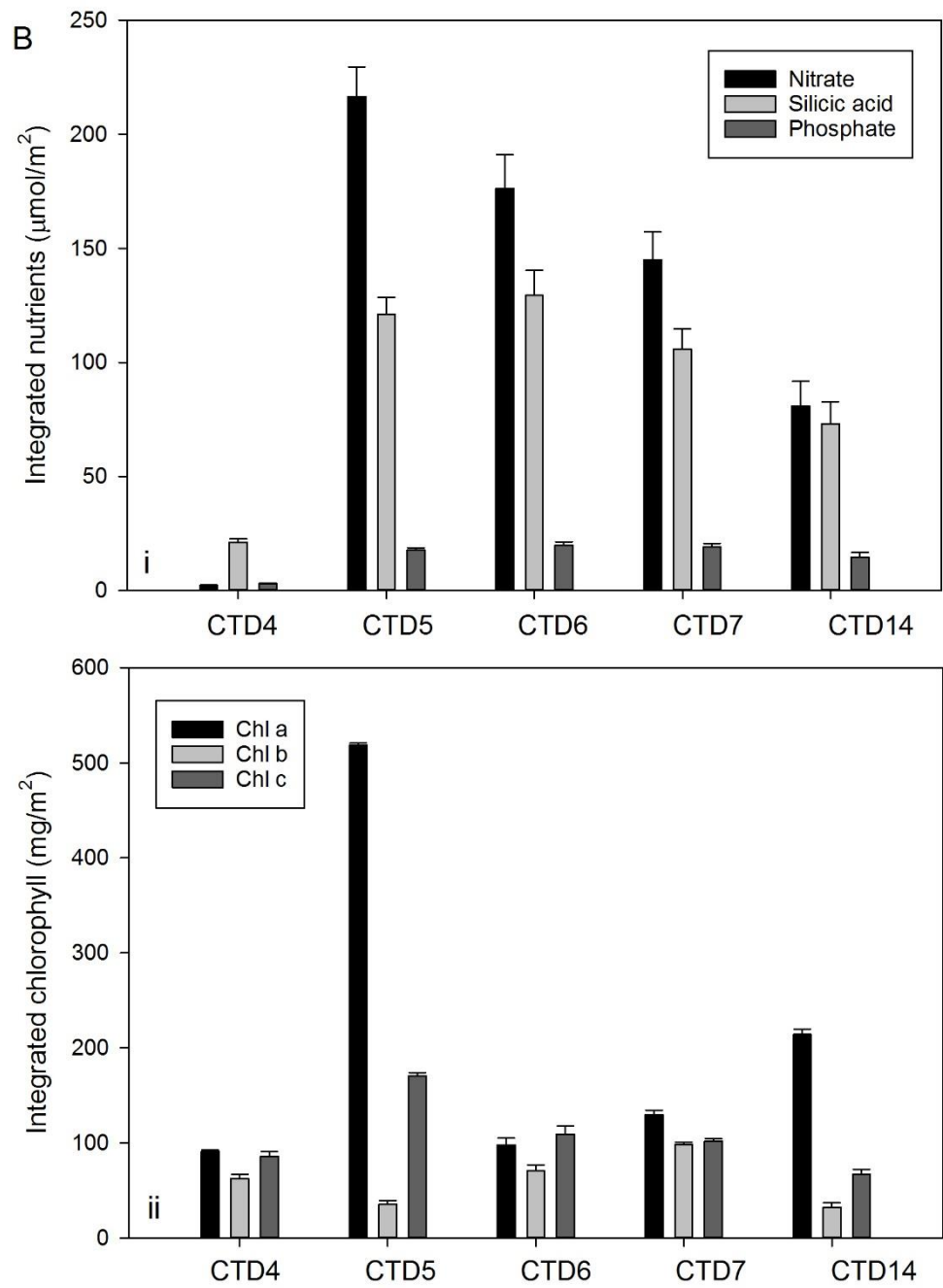
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855   Figure A1. Maps showing DY081 mega core (MGA) and ROV push core sites where pore-fluid

856   samples were taken, and cruise track (black line). Bathymetry resolution of the sampling

857   regions were improved with shipboard multibeam survey. Circles marking the core locations

858   have the same colours corresponding to those denoting the core identities in Figure 5.

859

Figure A2: A) Example cross section of macronutrient concentrations from the northern section of the Nuuk grid (from CTD 4,5,6,7,14, see Figure 2), showing (from top to bottom): nitrite, nitrate+nitrite, silicic acid, and phosphate (all in μM). This section encompasses the margin from the slope onto the shelf, and did not occupy the bathymetric trough (c.f. Figure 3, main text).
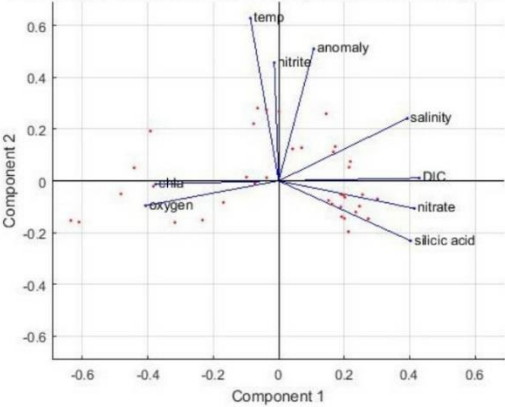
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867

B) Example cross section of integrated (top 50m) macronutrient and algal pigment
concentrations from northern section of the Nuuk grid (from CTD 4 to CTD 7, 14, see Figure
2). i) Integrated macronutrients; ii) Integrated pigment concentrations. Error bars show
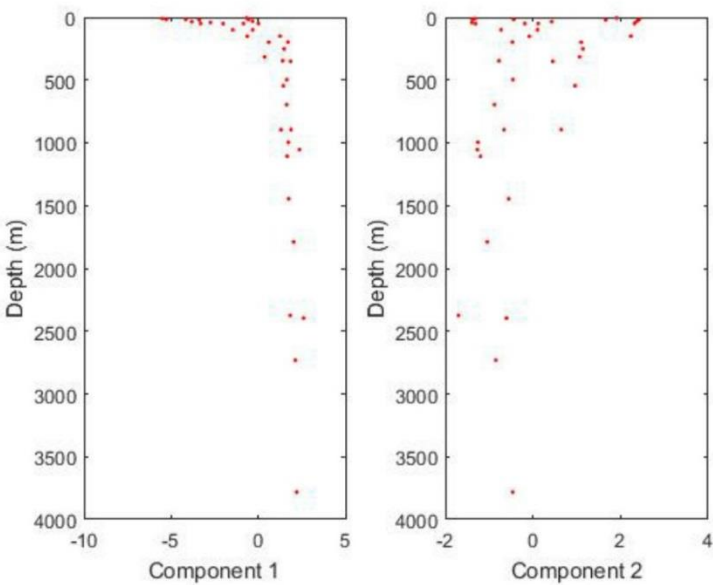propagated errors on integration calculation (1SD).

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873

A. Calculation one
Salinities set as per d¹⁸O mass balance (see main text)
Meteoric water alkalinity = 1000
Seawater alkalinity = 2312
Sea-ice alkalinity = 175
(Alkalinity in μmol/kg;
Data from Jones et al., 2008)

PCA analysis of meteoric water anomaly and environmental parameters

PC1 = 59%
PC2 = 17%
PC3 = 12%
Anomaly PC3 eigenvector <0.1

Anomaly = %Met$_{d18O}$- %Met$_{alk}$

B. Calculation two

Salinities set as per d¹⁸O mass balance (see main text)
Meteoric water alkalinity = 159
Seawater alkalinity = 2312
Sea-ice alkalinity = 175
(Alkalinity in μmol/kg;
Data from Meire et al., 2015;
Jones et al., 2008)
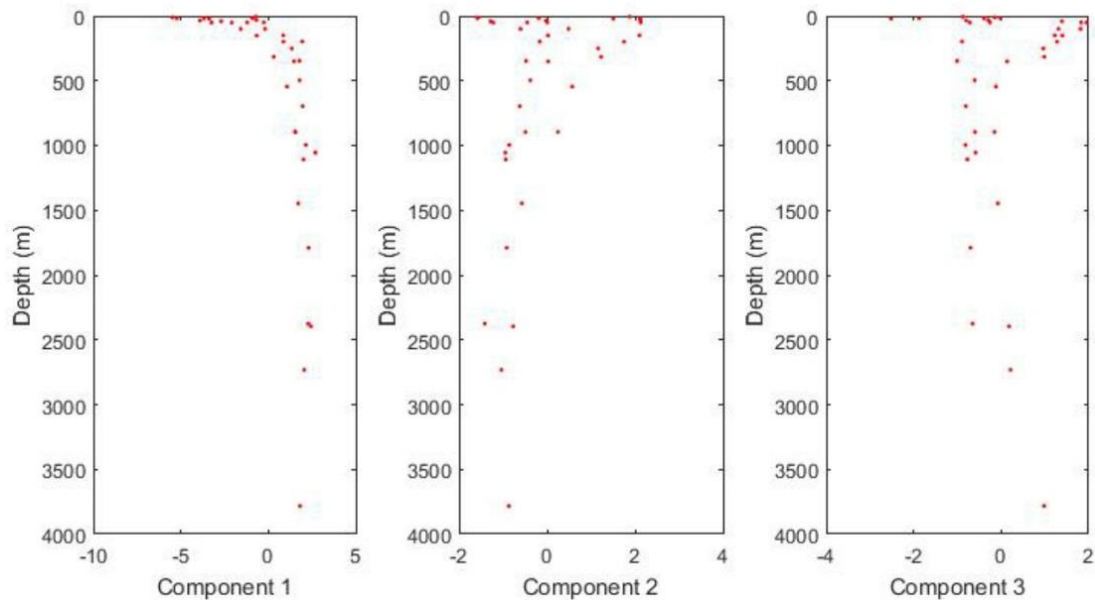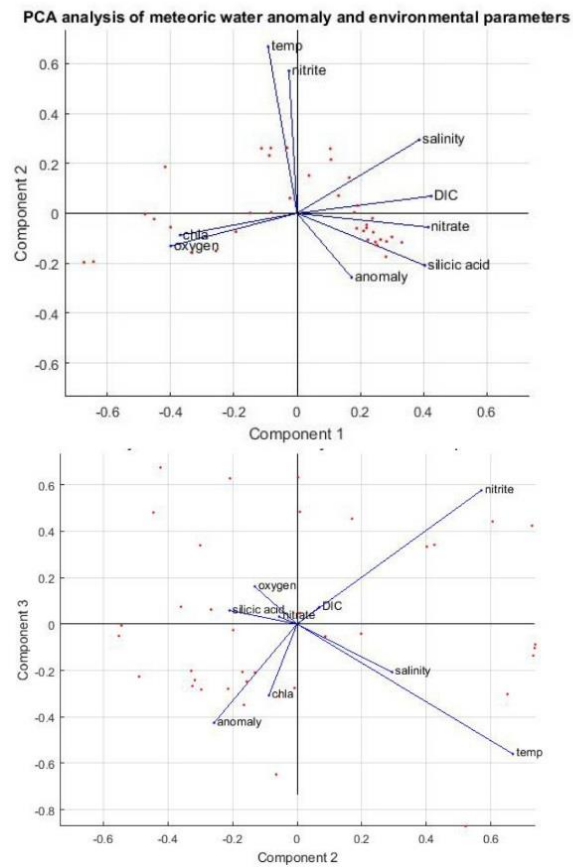
PC1 = 60%
PC2 = 15%
PC3 = 12%

Figure A3: Comparison of different freshwater mass balance calculations. Mass balance calculations were carried out using i) salinity and seawater $\delta^{18}O$ (see main text, Table 1), and ii) salinity and total alkalinity (TA) measurements:

42

$$F_{ir} + F_{me} + F_{si} = 1$$

$$F_{ir}S_{ir} + F_{me}S_{me} + F_{si}S_{si} = S_{ms}$$

$$F_{ir}A_{ir} + F_{me}A_{me} + F_{si}A_{si} = A_{ms}$$

Where F_{ir}, F_{me}, F_{si} are the calculated fractions of Irminger Water, meteoric and sea ice melt respectively (Irminger Water being the chosen ocean endmember), which sum to 1 by definition. They result is clearly dependent on the exact choice of endmembers for salinity (S_{ir}, S_{me}, S_{si}) and TA (A_{ir}, A_{me}, A_{si}) for the Irminger Water, meteoric and sea ice melt respectively. S_{ms} and A_{ms} are the measured salinity and TA of each sample. Two different calculations were carried out using different end-members for meteoric water alkalinity: A) 1000 μmol/kg (typical value for the Arctic Ocean, from Jones et al., 2008), and B) 159 μmol/kg (glacial meltwater value from Meire et al., 2015). This latter value is more likely to be a robust representation of the end-member in this region compared to the High Arctic as glacial meltwater is likely to dominated meteoric inputs.

The anomaly between the percentage meteoric water was then calculated using:

$$Anomaly = \%Met_{\delta 18O} - \%Met_{alk}$$

Principal Component Analysis was then carried out comparing this anomaly with other environmental parameters. Component loadings (lines) and scores (dots) for the main axes are shown (top) together with depth profiles of scores (bottom). Note that the %Met anomalies show strong loading with axes that also show high scores at subsurface depths, and correlate well with nitrite concentrations and temperature. This suggests that the anomalies arise as a result of non-conservative behaviour perhaps associated with water column nitrification or sedimentary denitrification.

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