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1 **Sediment efflux of silicon on the Greenland margin and**
2 **implications for the marine silicon cycle**

3

4

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17 **Abstract**

18 **The polar region is experiencing one of the most rapid environmental changes driven by**
19 **atmospheric warming, and feedbacks within the cryosphere. Under such a setting, it is crucial to**
20 **understand the biogeochemical cycling of the nutrient silicon (Si) in the high latitudes, which is**
21 **regulating the nutrient supply to polar ecosystems, and is linked to the global carbon cycle via**
22 **diatom production. However, these efforts have been hindered by a lack of understanding of**
23 **the benthic Si cycle, particularly the quantification of the sediment efflux of Si, and identification**
24 **of the responsible mechanistic processes during early diagenesis. Here, we address these issues**
25 **using new pore water profiles and incubation experiments on sediment cores collected from the**
26 **Greenland margin and Labrador Sea, combined with Si isotope analysis and a mass balance**
27 **model. Benthic Si flux at our study sites is found to be greatly heightened from values sustained**
28 **by pore water molecular diffusion. The remainder of the flux is likely accountable with early**
29 **dissolution of reactive biogenic silica phases at the upper sediments, and advective transport of**
30 **pore waters. Our results highlight an active benthic Si cycle at a northern high-latitude**
31 **continental margin, which could play a key role in recycling significant amounts of biologically**
32 **available dissolved Si to the overlying water, and influencing the growth of benthic and**
33 **planktonic communities in the polar region.**

34

35 **Keywords**

36 Polar ocean, benthic nutrient flux, ocean silicon cycle, silicon isotopes, early diagenesis.

37

38 **1. Introduction**

39 The global biogeochemical cycle of the nutrient silicon is a process that has received widespread
40 attention because it is coupled with the marine carbon cycle, which plays a crucial role in the

41 regulation of global climate. In particular, diatoms, a major phytoplankton group that builds
42 frustules by precipitating biogenic silica (BSi) from silicic acid (H_4SiO_4), the main form of dissolved
43 silica (DSi) in the water column, is a key modulator of the atmospheric level of primary greenhouse
44 gas, carbon dioxide (CO_2). Diatoms are responsible for nearly half of the oceanic uptake of CO_2
45 (Nelson et al., 1995), and they are a fundamental component of the marine Si cycle, acting as a
46 main sink of Si to the deep ocean and sediments (Sutton et al., 2018). However, given that
47 seawater is undersaturated with respect to Si, over 95 % of the diatom BSi and those of other
48 planktonic silicifiers such as radiolarians and silicoflagellates, are eventually remineralised back to
49 DSi in the ocean (Tréguer and De La Rocha, 2013). Approximately one-third of the remineralisation
50 occurs upon sediment deposition (Tréguer and De La Rocha, 2013), resulting in a benthic Si flux,
51 i.e. an efflux of Si out of the sediment back to the overlying water (Frings, 2017).

52
53 Although benthic Si fluxes have been evaluated at different areas of the global ocean (Frings,
54 2017), a coherent explanation of its controls is yet to emerge. This is because we still lack a
55 comprehensive understanding of the existing data to be able to provide a detailed assessment of
56 its mechanistic processes. These processes include: molecular diffusion maintained by a DSi
57 gradient between sediment pore waters and overlying bottom seawater (Frings, 2017), pore water
58 mixing or advection (Janssen et al., 2005), and benthic macrofaunal activities such as bioturbation
59 and bio-irrigation (Devol and Christensen, 1993). In addition, the magnitude of benthic Si flux
60 further depends on the rate of dissolution of BSi in the sediment, which is governed by multiple
61 factors including: diatom species, bacterial activity, redox condition and sediment aluminium
62 content (Aller, 2014). Understanding benthic Si flux is an essential task before an accurate
63 examination of the marine Si cycle can be performed, as it accounts for a major portion of the
64 remineralisation of BSi in the ocean, which in turn contributes to the vast majority of DSi supply to

65 sustain the new growth of marine silicifying organisms such as diatoms (Tréguer and De La Rocha,
66 2013).

67

68 There have been in the past a distinct lack of benthic Si flux studies in the northern high latitudes.
69 A recent study has highlighted that the biogeochemical cycling of Si in this region has a significant
70 influence on the ocean Si budget (Hawkings et al., 2018). For example, physical and chemical
71 erosion of silicate bedrock stimulated by glacial action, such as that found in Greenland, gives rise
72 to the formation of amorphous silica (ASi) as a weathering product, which then rapidly dissolves in
73 seawater (Hawkings et al., 2017). Melting glaciers are hence a significant source of nutrient Si that
74 could contribute to enhancing the production of diatoms at downstream fjords and in the coastal
75 ocean (Arrigo et al., 2017; Meire et al., 2016). There is also a diverse range of siliceous sponges
76 found around the coasts of Canada, Greenland and in the Labrador Sea (Hendry, 2017; Murillo et
77 al., 2018), which helps to regulate the benthic cycling of Si in the region as they utilise bottom
78 water DSi to precipitate BSi in order to build into their skeletal elements known as spicules
79 (Maldonado et al., 2005).

80

81 The aim of this study is to quantify the benthic Si flux coming from sediments on the Greenland
82 continental margin and in the Labrador Sea. The approach taken here involved the acquisition of
83 pore water profiles to estimate the molecular diffusion flux of DSi at the sediment-water interface
84 (McManus et al., 1995), and the execution of incubation experiments (Hammond et al., 2004) on
85 sediment cores to measure the net efflux of Si out of the sediment. Si has three stable isotopes:
86 ^{28}Si , ^{29}Si and ^{30}Si , with their relative abundance approximately 92.2 %, 4.7 % and 3.1 %
87 respectively. These isotopes undergo kinetic fractionation during low temperature processes such
88 as chemical weathering, authigenic clay formation, and during biological uptake by siliceous
89 organisms (Sutton et al., 2018). Here, the Si isotopes are employed for the first time to study

90 benthic Si flux in a high-latitude setting, and our results reveal new insights about the relative
91 contribution of the multiple processes that contribute to the benthic Si flux at the study sites,
92 along with implications for its role in the biogeochemical cycling of Si in the high latitudes.

93

94 **2. Materials and methods**

95 *2.1. Study sites*

96 During the RRS Discovery expedition DY081 (July–August 2017), seven sets of short (<0.4 m)
97 sediment cores, DY081-MGA1 – DY081-MGA7, were collected from a range of water depths (519–
98 3721 m) from the continental margin of South West Greenland, and also from an open ocean
99 setting in the Labrador Sea (Fig. 1, Table 1). The sites covered a range of sediment types from fine-
100 grained muds to coarser-grained sands, with varying degrees of bioturbation (Table 1).

101

102 The core sites are subject to the influence of glaciers to varying extents. In particular, glacial flour
103 input (fine-grained particles generated by glacial erosion) could potentially be inferred from the
104 uranium-series isotopes ^{224}Ra and ^{228}Th that have lithogenic origin (Hendry et al., 2019b). Elevated
105 activity concentrations of the particle-reactive ^{228}Th ($\sim 5\text{--}10$ dpm m^{-3}) observed proximal to our
106 Greenland margin sites are consistent with the supply of glacial flour to the area (Hendry et al.,
107 2019b). Increasing concentrations of the more soluble, short-lived ^{224}Ra (from ~ 1 to 9 dpm m^{-3})
108 along the flow path of the West Greenland Current (WGC), provides evidence for the continual
109 addition of glacial flour to the WGC (Hendry et al., 2019b). WGC eventually mixes and subducts
110 with other water masses to form Labrador Sea Water, providing a potential pathway for glacial
111 flour to reach the deeper sites in the Labrador Sea (Hendry et al., 2019b).

112

113 Euphotic zone chlorophyll data (Chl *a*) obtained from DY081 expedition shows peak
114 concentrations ranging from ~2–19 mg m⁻³ at the time of sediment core sampling, consistent with
115 values observed during a summer phytoplankton bloom on the Greenland margin and in the
116 Labrador Sea (Arrigo et al., 2017). Summer bloom in the region is typically associated with
117 enhanced supply of nutrients derived from melting glaciers (Arrigo et al., 2017). There is also a
118 spatial difference in diatom productivity in the study area. For instance, elevated diatom
119 production rates have been observed on the western Greenland margin off Nuuk (~2–14 mmol Si
120 m⁻² day⁻¹), relative to the other sites (~0.1–5 mmol Si m⁻² day⁻¹) (Hendry et al., 2019b).

121

122 Based on the remotely-operated underwater vehicle (ROV) images from cruise DY081, there is a
123 spatial difference in the relative distribution of sponge groups in the study area. Greater
124 abundance of hexactinellid sponges are observed at the sites in the Labrador Sea. Meanwhile,
125 South-West Greenland margin is dominated by diverse demosponge communities, including
126 numerous encrusting sponges (Hendry, 2017).

127

128 *2.2. Field sampling*

129 The coring device employed was a mega (multi-) coring system from UK National Marine Facilities.
130 The system housed multiple plastic core tubes of 0.60 m length and 0.105 m internal diameter,
131 and it was used to acquire a set of eight ‘replicate’ short sediment cores (<0.4 m) at each of the
132 seven sites (MGA1–MGA7). The mega coring system was capable in preserving the sediment-
133 water interface during sediment core collection.

134

135 One of the cores was used for pore water sampling, after the overlying core-top water was
136 siphoned off. Rhizon filters of 0.15 µm pore size (Rhizosphere) attached to syringes were inserted
137 into the sediment cores through holes pre-drilled on the core tube to extract filtered pore water,

138 generally at 0.02 m sediment depth intervals. Another replicate core was used for incubation
139 experiments in a 4°C temperature controlled cold room following the setup described in
140 Hammond et al. (2004). The heights of the core-top water columns of MGA1–MGA7 ranged from
141 0.14–0.32 m at the beginning of incubations. A magnetic stirrer (one-inch long) held in a platform
142 (open to surrounding water) at the top of incubator was set to rotate at ~33 rpm to maintain
143 constant mixing of the water column, without resuspending the sediments. Core-top seawater
144 was sampled and filtered through 0.45 µm at approximately every 2 hours for 24 hours. There was
145 no observable activity of macrofaunal irrigation throughout the incubations. The pore water and
146 core-top water samples were filtered through different pore sizes: 0.15 and 0.45 µm respectively,
147 but a previous study suggested that these two pore sizes did not cause a significant difference in
148 marine dissolved Si analysis (Knefelkamp et al., 2007). Samples were stored in cool, dark
149 conditions prior to analysis, unless otherwise specified later.

150

151 Several small, pristine sponges (stalked sponge and encrusting sponges) attached on pebbles were
152 observed atop the sediment column of MGA5 upon core retrieval (Appendix Fig. A.1). They
153 remained inside the core tube until the end of incubation experiment. The sponges were then
154 retrieved and preserved in 95 % ethanol and stored in a freezer at -20°C for subsequent Si isotope
155 analysis (Section 2.4).

156

157 *2.3. Measurement of dissolved Si concentrations, [DSi]*

158 Pore water [DSi] was measured on-board and post-expedition in the University of Bristol with
159 molybdate-blue method (Strickland and Parsons, 1968) using a V-1200 Vis spectrophotometer.
160 Following the GO-SHIP procedures in Hydes et al. (2010), split portions of core-top water samples
161 were frozen at -20°C immediately after sampling. Prior to [DSi] measurements, samples were
162 defrosted in a warm water bath for 45 minutes, followed by equilibration to room temperature for

163 30–40 minutes. Core-top water [DSi] was analysed at the Plymouth Marine Laboratory using a
164 SEAL analytical AAll segmented flow colorimetric auto-analyser, as described in Woodward and
165 Rees (2001). Seawater certified nutrient reference materials (KANSO Technos Ltd. Japan) were
166 measured during the analysis to monitor analyser performance and to ensure quality control of
167 the final data. The analytical errors associated with the two methods above were 2–3 %.

168

169 *2.4. Si isotope analysis*

170 A clean laboratory sample preparation technique for pore water and core-top waters, prior to
171 instrumental analysis, involved the pre-concentration of Si using a Mg-induced co-precipitation
172 method broadly following Souza et al. (2012). Briefly, Mg(OH)₂ was precipitated by adding 1 M
173 NaOH (Titripur® Reag. Ph Eur grade) to the pH neutral samples in two steps. Precipitates were
174 washed by adding 0.001 M NaOH, centrifuging, and removing the supernatant three times, so as
175 to quantitatively remove excess cations and anions (mainly Na⁺, Cl⁻, SO₄²⁻, Ca²⁺ and K⁺). The final
176 precipitates were then dissolved with 6 M in-house distilled HCl from the Bristol Isotope Group
177 laboratory, and the resulting solutions were diluted with 18.2 MΩ Milli-Q water for subsequent
178 column chemistry.

179

180 Sample preparation method for the sponges were mainly based on Hendry et al. (2019a). Milli-Q
181 rinsed, air-dried sponge subsamples were cleaned with 30 % reagent grade H₂O₂, initially at room
182 temperature, then in two steps at 80° C in a water bath, with Milli-Q rinses in between. Further
183 cleaning of the sponges was carried out with concentrated HNO₃ (in-house distilled) followed by a
184 Milli-Q rinse, three times, before drying on a hotplate. Dry sponge spicules were weighed, and a
185 final HNO₃ clean was carried out, before drying. The spicules were then dissolved with 0.4 M NaOH
186 (Titripur® Reag. Ph Eur grade) on a hotplate at 100° C for 3 days.

187

188 The processed pore water, core-top water and dissolved sponge samples were passed through
189 cation exchange columns following the procedures of Georg et al. (2006), purifying the solution
190 prior to instrumental analysis. Briefly, polypropylene columns were filled with 1.8 ml Bio-Rad
191 AG50W-X12, 200-400 mesh cation exchange resin in H⁺ form, which were rinsed with in-house
192 distilled HCl and Milli-Q before the samples were loaded onto the columns. Milli-Q was then used
193 to elute any sample remaining in the column, resulting in final elutions of 3–4 ml of 1–2 ppm Si
194 solution.

195

196 Measurements of the Si isotopes (²⁸Si, ²⁹Si, ³⁰Si) were carried out at the Bristol Isotope Group
197 laboratory using a Thermo-Finnigan Neptune, multi collector-inductively coupled plasma-mass
198 spectrometer (MC-ICP-MS), where samples were introduced into the plasma using a CETAC PFA
199 spray chamber (wet plasma) and PFA nebuliser (100 ul min⁻¹). The MC-ICP-MS operating
200 conditions followed Hendry et al. (2016). For pore water and core-top water samples, solutions
201 were doped with H₂SO₄ (ROMIL UpA™) and HCl (in-house distilled) to reach the target excess
202 concentrations of 500 ppm for SO₄²⁻ and 3,500 ppm for Cl⁻ in order to alleviate the anionic matrix
203 effects (Hughes et al., 2011). Corrections for both instrumental mass bias and matrix effects were
204 carried out using standard-sample bracketing and Mg-doping methods (Cardinal et al., 2003).

205

206 Si isotope composition of a given material is typically expressed as δ³⁰Si values relative to the
207 international standard NBS-28 per mil (‰):

$$208 \quad \delta^{30}\text{Si} = \left[\frac{(^{30}\text{Si}/^{28}\text{Si})_{\text{sample}}}{(^{30}\text{Si}/^{28}\text{Si})_{\text{NBS-28}}} - 1 \right] \times 1000 \quad (1)$$

209 Replicate measurements of several reference standards (Table 2) were carried out to assess long-
210 term external reproducibility of the protocol, and the mean δ³⁰Si obtained for the standards agree
211 with published values within 2 SD (Table 2). Some replicate measurements were made on five

212 pore water samples (n = 2–3) (Fig. 2b, d & f), five core-top water samples (n = 2–3) (Fig. 3b), and
213 the sponge samples (n = 2–4) (Appendix data). The range of 2 SD obtained in these sample
214 replicate measurements are 0.06–0.28 ‰ for pore water, 0.0003–0.19 ‰ for core-top water, and
215 0.14–0.25 ‰ for sponge. The $\delta^{29}\text{Si}$ and $\delta^{30}\text{Si}$ values of all standards and samples measured during
216 this study plot on a straight line (Appendix Fig. A.2) through the origin with a gradient of $0.5181 \pm$
217 0.0040 , which lies between thermodynamic (0.5210) and kinetic (0.5105) mass-dependent
218 fractionation (Cardinal et al., 2003).

219

220 *2.5. Pore water dissolved major and trace element concentration measurement*

221 Split portions of pore water samples were acidified by adding 1 % v/v 10 M in-house distilled HCl,
222 and were left to equilibrate for at least three months prior to dissolved concentration
223 measurements of selected elements. Major elements: [K] and [Mg] were analysed with inductively
224 coupled plasma-optical emission spectroscopy (ICP-OES) using an Agilent 710 instrument at the
225 University of Bristol. Trace elements: [Al], [Fe], and [Mn] were analysed using an Agilent 8800
226 inductively coupled plasma-triple quadrupole-mass spectrometer (ICP-QQQ-MS) at the Open
227 University. Monitoring of analyser performance was carried out on both instruments with periodic
228 measurements of blanks and calibration standards. Data quality of the low concentration trace
229 elements was further constrained with the analysis of a river water (SLRS-6) and a nearshore
230 seawater (CASS-6) certified reference material. [Al], [Fe] and [Mn] measurements of these
231 reference standards agree well with certified values within 95 % confidence interval.

232

233 *2.6. Calculation of benthic Si flux*

234 Benthic flux of Si from the sediment to the overlying bottom water at each study site was
235 evaluated using two methods: (1) pore water [DSi] profile, and (2) core-top water [DSi] from the
236 incubation experiment. Molecular diffusion flux, $J_{\text{diffusion}}$ ($\text{mmol m}^{-2} \text{day}^{-1}$), through the sediment-

237 water interface was estimated by combining Fick's First Law of Diffusion, and exponential fitting of
238 the pore water [DSi] profile (McManus et al., 1995) (Fig. 2a, c, & e):

$$239 J_{\text{diffusion}} = \phi_0 \times (D_m/\theta^2) \times \beta \times (C_d - C_0) \quad (2)$$

$$240 C_z = C_d - (C_d - C_0) \times e^{-\beta z} \quad (3)$$

241 ϕ_0 is the core-top sediment porosity; θ^2 is the tortuosity; D_m ($\text{m}^2 \text{day}^{-1}$) is the molecular diffusion
242 coefficient for silicic acid in free solution; β (m^{-1}) expresses the curvature of the exponential
243 profile, which reflects the depth at which pore water DSi approaches asymptotic concentrations,
244 C_d (mmol m^{-3}); C_0 (mmol m^{-3}) is the ambient core-top water [DSi]; C_z (mmol m^{-3}) is pore water [DSi]
245 at a given sediment core depth, z (m).

246

247 The values of the parameters used to calculate $J_{\text{diffusion}}$ for MGA1–MGA7 are listed in Table 3, and
248 the uncertainties associated with $J_{\text{diffusion}}$ was propagated from all analytical errors (Table 3). The
249 potential presence of a diffusive boundary layer at the sediment-water interface, typically
250 possessing a thickness of 0.2–1 mm (Schulz and Zabel, 2006), was not explicitly accounted for. This
251 might cause minor underestimation of C_0 , and might therefore lead to slight overestimation of the
252 calculated $J_{\text{diffusion}}$ (McManus et al., 1995), but the effect was expected to be small relative to the
253 uncertainties associated with the other parameters (Table 3) used to derive $J_{\text{diffusion}}$ (McManus et
254 al., 1995).

255

256 The apparent total benthic Si flux, J_{total} , was evaluated based on the rate of change of core-top
257 water [DSi] in the core incubation (Hammond et al., 2004). During the incubation, the height of the
258 core-top water column, h , decreased after each sampling interval. The decrease in h led to
259 systematic bias in the rate of change of core-top water [DSi] (Hammond et al., 2004). Correction
260 for this bias was made by fitting a linear regression to a plot of measured core-top water [DSi]
261 (mmol m^{-3}) against the ratio of incubation time to h , t/h (day m^{-1}) (Hammond et al., 2004) (Fig. 3c).

262 The slope of the regression was J_{total} ($\text{mmol m}^{-2} \text{day}^{-1}$), and the uncertainty associated with J_{total}
263 was directly derived from the error of the slope (Fig. 3c).

264

265 The flux calculations above were not corrected for temperature effects on adsorption/desorption
266 of Si onto sediment particles or dissolution rates of BSi (Hammond et al., 2004). This was because
267 core incubations were carried out at a temperature close to those of in-situ bottom water at the
268 core sites (2–4°C). Sampling of pore waters were carried out at room temperature, but they were
269 done within 10 hours of sediment core retrievals, which was a timeframe where no critical change
270 in pore water [DSi] profile was observed, as shown in a previous experiment (Hendry et al.,
271 2019b).

272

273 **3. Results and Discussion**

274 *3.1. Pore water data and early diagenesis of Si*

275 Pore water [DSi] data from MGA1–MGA7 have been presented elsewhere (Hendry et al., 2019b).

276 Overall, pore water [DSi] and $\delta^{30}\text{Si}$ observed here range from 76 to 616 mmol m^{-3} (unit equivalent
277 to μM) and +0.76 to +2.08 ‰ respectively. The down-core trends of pore water [DSi] at all of our
278 sites could generally be described with exponential profiles, where [DSi] broadly increases with
279 increasing core depths at ever decreasing rates towards asymptotic values (Fig. 2a, c & e).

280

281 The pore water profiles of [DSi] and $\delta^{30}\text{Si}$ reflect early diagenesis of Si that is occurring in the
282 marine sediments. For instance, the observed increases in pore water [DSi] (Fig. 2a, c & e) are
283 primarily associated with dissolution of reactive silica phases (Aller, 2014). The pore water Si
284 isotope data might provide further insights on some of the more distinct constituents: diatom BSi,
285 sponge BSi, and glacial ASi, that all contribute to the increases in pore water [DSi], based on their

286 different isotopic compositions. The diatom BSi at our study sites is expected to have relatively
287 high $\delta^{30}\text{Si}$: broadly greater than +1.5 ‰, following existing measurements in the northern high-
288 latitude ocean (Varela et al., 2016). Indication of high DSi utilisation in the study area is supported
289 by a recent study, which has found active diatom production that consumes around 4–10 % of the
290 euphotic zone DSi inventory daily (Hendry et al., 2019b). Such high DSi utilisation provides further
291 evidence for relatively positive diatom $\delta^{30}\text{Si}$ at our sites, given the progressive enrichment of ^{30}Si in
292 the euphotic zone DSi inventory utilised for BSi formation (de la Rocha et al., 1997). In contrast,
293 sponge BSi has lighter $\delta^{30}\text{Si}$, mainly less than 0 ‰ (Hendry et al., 2019a), while the glacial ASi has
294 been recently found to have $\delta^{30}\text{Si}$ in the range of -0.5 to -0.2 ‰ (Hatton et al., 2019; Hawkings et
295 al., 2018).

296

297 MGA6 and MGA4 generally exhibit down-core decreases in pore water $\delta^{30}\text{Si}$ towards values lowest
298 at +0.76 ‰ (Fig. 2f) and +1.05 ‰ (Fig. 2d) respectively, and at MGA7 pore water $\delta^{30}\text{Si}$ is evidently
299 reduced (+1.10 to +1.26 ‰) relative to its overlying core-top water (+1.58 ‰) (Fig. 2f). Assuming
300 there is no Si isotope fractionation during BSi/glacial ASi dissolution, these observations
301 potentially reflect a relative increase in the dissolution of endmembers with the lighter Si isotope
302 composition: sponge BSi and glacial ASi in MGA4, MGA6 and MGA7. In contrast, pore water $\delta^{30}\text{Si}$
303 in MGA1, MGA2, MGA3 and MGA5 are elevated overall relative to their overlying core-top water
304 values, and are generally at around or higher than +1.5 ‰ (Fig. 2b, d & f), which are in the range of
305 $\delta^{30}\text{Si}$ of diatom BSi inferred for the core sites. Therefore, dissolution of diatom BSi might have
306 contributed to the pore water $\delta^{30}\text{Si}$ observations in these four cores.

307

308 A previous study has shown some evidence of reverse weathering in Arctic sediments (März et al.,
309 2015). Reverse weathering generally refers to the formation of authigenic clays from (dissolving)
310 BSi, reactive Al and Fe (oxyhydroxides or their dissolved forms), and major cations dissolved in

311 pore water especially K and Mg (Aller, 2014; Michalopoulos and Aller, 2004). Precipitation of
312 authigenic clays has been suggested to preferentially incorporate the lighter Si isotopes resulting
313 in a heavier isotopic composition in the pore water (Ehlert et al., 2016).

314

315 Combined pore water $\delta^{30}\text{Si}$ and elemental concentration data might provide an indication of
316 reverse weathering taking place in some of our cores. For example, strong down-core reductions
317 of pore water [K] and [Mg] observed in MGA5 (Fig. 4c) are consistent with uptake of the dissolved
318 cations by reverse weathering. MGA5 pore water [DSi] and $\delta^{30}\text{Si}$ profiles (Fig. 2e & f) might be
319 reflecting a balance between multiple diagenetic processes, including reverse weathering and
320 BSi/glacial ASi dissolution. Peaks of pore water [Al] observed (up to 3.2 mmol m^{-3}) from $\sim 0.15\text{--}0.30$
321 m core depth of MGA3 (Fig. 4b) might suggest increased availability of reactive Al, which could
322 enhance rates of reverse weathering. This is in agreement with pore water $\delta^{30}\text{Si}$ increase (Fig. 2d)
323 and [Mg] decrease (Fig. 4b) observed at the same MGA3 core depth interval. However, a
324 corresponding pore water [K] decrease is not observed (Fig. 4b), perhaps implying the formation
325 of authigenic clays that differ from the typical reverse weathering reactions shown in previous
326 studies (Aller, 2014; Michalopoulos and Aller, 2004).

327

328 Diagenesis of Si has also been linked to sediment redox conditions, mainly via oxidative-
329 precipitation and reductive-dissolution of Fe oxyhydroxides (Aller, 2014). Overall, elevated levels
330 of pore water [Fe] (up to 72 mmol m^{-3}) in MGA3–MGA6 (Fig. 4) are indicative of bacteria-mediated
331 reductive dissolution of Fe oxyhydroxides, reflecting anoxic conditions in these cores (Aller, 2014).
332 Down-core decrease in MGA4 pore water [Fe] (Fig. 4b) most likely is associated with the
333 precipitation of reduced Fe forming iron sulphides (Aller, 2014). Interestingly, MGA3–MGA6 also
334 exhibit overall higher levels of pore water [DSi] than the other cores (Fig. 2a, c & e). This
335 observation is consistent with both desorption of Si from Fe oxyhydroxide following its reductive

336 dissolution, and increased BSi solubility after losing Fe oxyhydroxide coatings in anoxic sediments,
337 lending support to the role of sediment Fe cycling in regulating pore water [DSi] (Aller, 2014).
338 However, there is no obvious link between the MGA cores' pore water [Fe] (Fig. 4) and $\delta^{30}\text{Si}$ (Fig.
339 2b, d & f) profiles, suggesting that redox-driven sediment Fe cycling might not have imposed a
340 clear Si isotope signal on the pore waters compared to the other diagenetic activities.

341
342 Our pore water results have shown a mix of diagenetic processes that play a role in regulating
343 pore water DSi (and $\delta^{30}\text{Si}$), which include dissolution of diatom BSi, sponge BSi and glacial ASi,
344 reverse weathering, and redox cycling of Fe. Marine silicate weathering is also a potential process
345 that might supply DSi to the pore water (Tréguer and De La Rocha, 2013). The net effects of these
346 processes are the exponential pore water [DSi] profiles (Fig. 2a, c & e), which give rise to molecular
347 diffusion fluxes that contribute to the net effluxes of Si out of the sediments into the overlying
348 seawater. These diffusion fluxes will carry distinct Si isotopic signatures imposed by the multiple
349 diagenetic processes described above.

350

351 *3.2. Core incubation results and rapid sponge dissolution*

352 All core-top water [DSi] concentrations, over the entire incubation period, range from 6.8 to 24.7
353 mmol m^{-3} . The core-top water [DSi] exhibits a linear increase with time in all incubation
354 experiments (Fig. 3a), indicating net positive effluxes of Si out of the sediment into the overlying
355 bottom water at all study sites, regardless of water depths or marine settings. Whilst the relative
356 trends through time are consistent, there is a significant variation in the absolute gradient of core-
357 top water [DSi] increase against incubation time between the core locations (Fig. 3a). Such
358 variation reflects a spatial difference in the magnitude of sediment efflux of Si in the study area,
359 and this is further evaluated in Section 3.3.

360

361 MGA1, MGA2, MGA4 and MGA7 display minor changes in core-top water $\delta^{30}\text{Si}$ over the incubation
362 period. Both MGA3 and MGA6 core-top waters show gradual but statistically significant ($p < 0.05$)
363 linear increases in $\delta^{30}\text{Si}$ from +1.29 to +1.66 ‰, and +1.36 to +1.55 ‰ respectively, during the
364 incubation experiment (Fig. 3b). The gradual $\delta^{30}\text{Si}$ increase likely reflects continual dissolution of
365 diatom BSi (which likely has $\delta^{30}\text{Si}$ signature of greater than +1.5 ‰ for our sites, see Section 3.1) at
366 the uppermost sediment layers of MGA3 and MGA6. Contrary to the above, MGA5 core-top water
367 exhibits a pronounced decrease in $\delta^{30}\text{Si}$ from +1.27 to +0.18 ‰ during the incubation (Fig. 3b).

368

369 One stalked sponge and four encrusted sponges found attached on pebbles atop the sediment
370 column of MGA5 show average $\delta^{30}\text{Si}$ ranging between -1.02 and -1.45 ‰ (Fig. 3b). The significant
371 decrease of MGA5 core-top water $\delta^{30}\text{Si}$ towards observed sponge values, along with the
372 considerable increase of its [DSi] (Fig. 3) are indicative of substantial remineralisation of the
373 sponge individuals that were found atop the sediment column at this South West Greenland site,
374 even before sediment burial. Our results suggest that under certain conditions sponge spicules
375 have considerable dissolution rates, contrary to the findings of a previous study (Maldonado et al.,
376 2005), which showed no detectable dissolution of sponge spicules for at least 14 days. This
377 discrepancy could be related to the spicule structure, spicule size or the degree of sponge
378 silicification (Bertolino et al., 2017; Conley and Schelske, 1993). The more lightly silicified
379 encrusting sponges, and the stalked sponge presented here, might have structural properties that
380 are more susceptible to dissolution than sponges that have been previously investigated
381 (Maldonado et al., 2005).

382

383 Overall, sponges act as a net sink of Si through the precipitation of BSi from bottom water DSi to
384 build spicules, which are subsequently buried in the sediments (Tréguer and De La Rocha, 2013).
385 However, these new results highlight the significance of sponge BSi remineralisation even prior to

386 sediment burial, which suggests that spicule dissolution could be a net contributor to benthic Si
387 flux in certain continental margin settings. Our findings also imply that spicule dissolution rates
388 may vary between different sponge species (Bertolino et al., 2017), in addition to the variation in
389 their DSi uptake rates during growth (López-Acosta et al., 2018).

390

391 *3.3. Benthic Si flux processes*

392 Based on the pore water [DSi] profiles, the estimated molecular diffusion fluxes of Si, $J_{\text{diffusion}}$, for
393 MGA1–MGA7, across the sediment-water interface, range between 0.06 and 0.32 mmol m⁻² day⁻¹.

394 In contrast, the total effluxes of Si from the sediment into the overlying bottom water, J_{total} , when
395 directly measured from the core incubation experiments, are larger in magnitude (Fig. 5). There is

396 a substantial variation in J_{total} across the study sites, ranging between 0.31 and 3.08 mmol m⁻² day⁻¹.

397 ¹. Using the calculated fluxes, a mass balance of benthic Si flux can be developed for our study

398 sites:

$$399 J_{\text{total}} = J_{\text{diffusion}} + (J_{\text{sponge}}) + J_{\text{residual}} \quad (4)$$

400 J_{residual} is defined as the residual benthic Si flux that is not accounted for by $J_{\text{diffusion}}$, and pre-burial
401 sponge dissolution, J_{sponge} , for MGA5. For all the other sites, J_{residual} is derived by subtracting $J_{\text{diffusion}}$

402 from J_{total} at each site, and this ranges between 0.13 and 1.74 mmol m⁻² day⁻¹ (Table 4). For MGA5,

403 we assume that J_{residual} is similar to nearby sites: MGA6 and MGA7, and the benthic flux associated

404 with J_{sponge} is then estimated by subtracting $J_{\text{diffusion}}$ and the inferred J_{residual} from the J_{total} of the

405 site. J_{sponge} at MGA5 is found to be 2.53 mmol m⁻² day⁻¹ (Table 4).

406

407 Rapid remineralisation of BSi in the uppermost sediment layer coupled with a non-steady state

408 condition in the pore water (Schulz and Zabel, 2006) is a likely contributing factor to J_{residual} . The

409 sediment cores were collected during the summer bloom period (Section 2.1). The pore water

410 [DSi] profiles might not have sufficient time to respond to the recent enhanced deposition of fresh
 411 diatom BSi from the summer bloom, giving rise to the offset between the pore water-derived
 412 $J_{\text{diffusion}}$ and core incubation-derived J_{total} . Rapid remineralisation of freshly deposited BSi might be
 413 consistent with the overall low sediment BSi(/ASi) content (0.04–0.56 weight %) observed in
 414 several cores: MGA2, MGA3, MGA5, MGA6 and MGA7 (Appendix Fig. A.3). In addition, it might be
 415 possible for the stirring of core-top water column during the incubation experiment (Section 2.2)
 416 to drive movement of water through permeable upper sediments (Janssen et al., 2005), such as
 417 those in MGA2 and MGA3 that are mainly composed of sandy sediment (Table 1). If true, the
 418 resulting pore water advection might lead to a net transport of Si to the overlying water column,
 419 contributing to J_{residual} in these two cores.

420

421 Further evaluation on the multiple processes that constitute benthic Si flux can be carried out by
 422 constructing the isotopic mass balance, which assumes no Si isotope fractionation during
 423 BSi/glacial ASi dissolution:

$$424 \frac{d(C \cdot \delta^{30}\text{Si}_{\text{core-top water}})}{d(t/h)} = J_{\text{diffusion}} \cdot \delta^{30}\text{Si}_{\text{diffusion}} + (J_{\text{sponge}} \cdot \delta^{30}\text{Si}_{\text{sponge}}) + J_{\text{residual}} \cdot \delta^{30}\text{Si}_{\text{residual}} \quad (5)$$

425 $\frac{d(C \cdot \delta^{30}\text{Si}_{\text{core-top water}})}{d(t/h)}$ (values in Table 4) is the derivative of the product between core-top water
 426 [DSi] and its isotopic composition with respect to the t/h parameter (definition in Section 2.6). The
 427 shallowest available pore water $\delta^{30}\text{Si}$ is used as an approximate representation of $\delta^{30}\text{Si}_{\text{diffusion}}$, the
 428 isotopic signature associated with molecular diffusion flux (Table 4). $\delta^{30}\text{Si}_{\text{sponge}}$ is the average
 429 isotope composition of sponges found atop the sediment column of MGA5 (Table 4). This equation
 430 could be used to estimate $\delta^{30}\text{Si}_{\text{residual}}$, which represents the integrated isotopic signature of the
 431 endmember(s) responsible for J_{residual} . The isotopic mass balance has not accounted for back
 432 diffusion of core-top water DSi into sediment pore water, but the effect should be minimal given
 433 the much lower [DSi] in core-top water.

434

435 The calculated $\delta^{30}\text{Si}_{\text{residual}}$ for MGA1, MGA2, MGA3, MGA4, MGA6 and MGA7 range between +1.47
436 and +1.76 ‰ (Table 4). If J_{residual} is mainly attributed to the rapid remineralisation of freshly
437 deposited diatom BSi (with non-steady state condition in pore water), then $\delta^{30}\text{Si}_{\text{residual}}$ might
438 largely reflect the isotopic signature of diatom BSi. The $\delta^{30}\text{Si}_{\text{residual}}$ of MGA2 and MGA3 might also
439 have some mixed isotopic signals advected from pore waters in the permeable upper sediments.
440 For MGA5, the calculated $\delta^{30}\text{Si}_{\text{residual}}$ (+2.71 ‰) is evidently higher than the other sites (Table 4),
441 which might imply the influence of sea-ice diatoms that could have heavy Si isotope composition
442 (Varela et al., 2016). Alternatively, such a difference might be attributed to the underestimation of
443 J_{residual} at MGA5, which has been assumed to be similar to MGA6 and MGA7; and to the potential
444 of rapid authigenic clay formation in the upper sediments.

445

446 Spatial variation in benthic Si flux between the study sites can be seen more clearly with the
447 isotopic mass balance model. The highest flux recorded at MGA5 ($3.08 \text{ mmol m}^{-2} \text{ day}^{-1}$) is largely
448 (~82 %) due to rapid dissolution of sponges (Fig. 5, Table 4). The second largest flux is observed in
449 a core from the western Greenland margin: MGA3 ($1.87 \text{ mmol m}^{-2} \text{ day}^{-1}$) (Fig. 5, Table 4), with a
450 significant portion of it possibly attributed to remineralisation of seasonally intensified diatom BSi
451 deposition at the uppermost sediment layer. This is potentially consistent with the higher diatom
452 production rates ($\sim 2\text{--}14 \text{ mmol Si m}^{-2} \text{ day}^{-1}$) found in the vicinity of MGA3 core site (Hendry et al.,
453 2019b). Our results also open the possibility for pore water advection (through permeable upper
454 sediments) to contribute to benthic Si flux in core MGA2 and MGA3, not just in incubation
455 experiment, but also under natural environmental condition. This is because pore water advection
456 could be caused by horizontal advection of bottom currents over uneven sediment surface
457 (Janssen et al., 2005; Schulz and Zabel, 2006), and active bottom currents are potentially present
458 on the Greenland margin (Hendry et al., 2019b) and in the Labrador Sea (Handmann et al., 2018).

459 Sediment bio-irrigation is another process that could contribute to benthic Si flux, as burrowing
460 macrofauna could flush DSi-enriched pore water to the overlying seawater (Devol and
461 Christensen, 1993; Hammond et al., 2004). This process was likely under-represented in our core
462 incubation, where minimal benthic macrofaunal activity was observed.

463

464 *3.4. New interpretations of benthic Si flux in northern high latitudes, and the global ocean*

465 We have produced a new compilation of global benthic Si flux to include our data (Fig. 6). This
466 compilation is more inclusive than previously reported (Frings, 2017), as we also include direct
467 measurements of total benthic Si fluxes, J_{total} (Fig. 6b), with the core incubation and benthic
468 chamber methods (Hammond et al., 2004), in addition to diffusive benthic Si fluxes, $J_{\text{diffusion}}$ (Fig.
469 6a) (Frings, 2017). $\Delta J_{\text{total-diffusion}}$, the difference between J_{total} and $J_{\text{diffusion}}$, have also been calculated
470 when both values have been evaluated at the same or proximal sites (<15 km distance apart).
471 Overall, we find a range of $\Delta J_{\text{total-diffusion}}$ from -0.8 to +13.5 mmol m⁻² day⁻¹ (Fig. 6c). The
472 mechanisms proposed to explain our results from the Greenland margin and Labrador Sea might
473 also contribute to the interpretation of the global $\Delta J_{\text{total-diffusion}}$ observations.

474

475 For instance, non-steady state condition in pore water arised from seasonal variation in BSi
476 deposition might lead to either positive or negative $\Delta J_{\text{total-diffusion}}$ at different times of the year(s)
477 (Schulz and Zabel, 2006), and might explain some of the observed range above (Fig. 6c).

478 Alternatively, sites with negative fluxes might reflect increased rates of benthic DSi removal by
479 processes such as sponge uptake and authigenic clay formation. Interestingly, some of the highest
480 J_{total} and $\Delta J_{\text{total-diffusion}}$ are consistently observed at continental margins (Fig. 6b & c), including those
481 proximal to estuarine and deltaic settings, where rapid rates of reverse weathering are expected
482 (Tréguer and De La Rocha, 2013). Further explanation of these observations might rely on other
483 non-diffusive processes. For example, there could be: increased sediment bio-irrigation (Devol and

484 Christensen, 1993) at productive margins due to greater abundance of burrowing benthic
485 organisms, enhanced pore water advection in continental shelf sediments that are subjected to
486 high energy bottom currents (Janssen et al., 2005), and pre-burial rapid dissolution of certain
487 sponge group. Our compilation highlights that benthic Si flux is not solely maintained by diffusion
488 of pore water DSi at certain settings, which has important implications for existing evaluations of
489 the oceanic Si budget that have implicitly made such an assumption (Frings, 2017; Tréguer and De
490 La Rocha, 2013).

491

492 Our compilation also reveals that the benthic Si flux observed at the high-latitude continental
493 margins is relatively significant in magnitude – generally larger than the open ocean sites, though
494 smaller than the low-latitude marginal sites (Fig. 6b). Strong benthic fluxes might be particularly
495 important for the western Greenland margin, where wind-driven coastal upwelling takes place.
496 Previous studies provide some indications that episodes of northerly wind events in this region
497 (Dumont et al., 2010; Hvid Ribergaard et al., 2004) could upwell waters from hundreds of meters
498 depths (Dumont et al., 2010), which potentially cover the depth range of western Greenland
499 continental shelf (<725 m) (Gougeon et al., 2017). Therefore, sediment efflux of Si from western
500 Greenland shelf could get entrained in the upwelling water mass and become a source of this
501 nutrient to the coastal surface ocean. The range of J_{total} (Fig. 5) derived from our continental shelf
502 sites (Fig. 1) MGA4 and MGA5 might provide a preliminary estimate of benthic Si flux from the
503 western Greenland shelf. Given the region's approximate area of 0.24 Tm^2 (from $75\text{--}60^\circ \text{N}$, with
504 shelf break depth of $\sim 200\text{--}700 \text{ m}$ (Gougeon et al., 2017)), total sediment efflux of Si from western
505 Greenland shelf is estimated to be $0.15 (0.04\text{--}0.27) \text{ Tmol year}^{-1}$. This is in the same order of
506 magnitude as the continental inputs of Si in the northern high latitudes – previous estimates of
507 total Si export from Greenland Ice Sheet and the pan-Arctic rivers are 0.2 and $0.35 \text{ Tmol year}^{-1}$
508 respectively (Hawkings et al., 2017).

509

510 Based on the estimation above, benthic flux is most likely a significant source of nutrient Si that
511 contributes to sustaining both the diverse (benthic) sponge communities (Hendry, 2017), and the
512 enhanced levels of (planktonic) diatom productivity ($\sim 2\text{--}14 \text{ mmol Si m}^{-2} \text{ day}^{-1}$) (Hendry et al.,
513 2019b) observed at the western Greenland margin. Interestingly, surface water [DSi] of the region
514 is very low ($<5 \text{ mmol m}^{-3}$) (Hendry et al., 2019b). These combined observations support the notion
515 of a rapid and highly-tuned pelagic-benthic recycling of Si on the Greenland margin, where
516 sediment efflux might be supplying the remineralised nutrients back to the deep and surface
517 ocean, which are then rapidly utilised through new sponge and phytoplankton growth. Similar
518 processes might take place at other coastal upwelling sites in the Arctic region, and the proposed
519 scenario is consistent with the presence of active biogeochemical cycling of Si in the northern
520 high-latitude ocean margins.

521

522 **4. Conclusions**

523 The pore water [DSi] and $\delta^{30}\text{Si}$ data from the Greenland margin and Labrador Sea reflect a mix of
524 diagenetic activities, which include: the dissolution of diatom BSi, sponge BSi and glacial ASi,
525 reverse weathering, and the redox cycling of Fe. The net effects of these processes are the
526 exponential pore water [DSi] profiles which give rise to molecular diffusion fluxes. However, the
527 core incubation data suggests that diffusion flux alone could not account for the total sediment
528 efflux of Si to the overlying water column. Using our new data, we present the first Si isotope mass
529 balance model, which is a potential tool for the identification and evaluation of the nature and
530 relative magnitude of the different processes that contribute to benthic Si flux in a glaciated
531 environment. Results provide supporting evidence for multiple mechanisms that could contribute
532 to the remainder of benthic Si fluxes at our high-latitude sites. These mechanisms include: pre-
533 burial rapid dissolution of certain sponge group, seasonally intensified deposition of fresh diatoms

534 in the uppermost sediments coupled with a non-steady state condition in pore water, and pore
535 water advection. This study also reveals that the benthic Si fluxes at the northern high-latitude
536 continental margins are overall higher than those in the open ocean. In particular, we find that
537 strong benthic fluxes are likely recycling substantial amounts of Si to sustain new sponge and
538 phytoplankton growth at the western Greenland margin, lending support to the presence of active
539 biogeochemical cycling of Si in the northern high-latitude ocean margins.

540

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551

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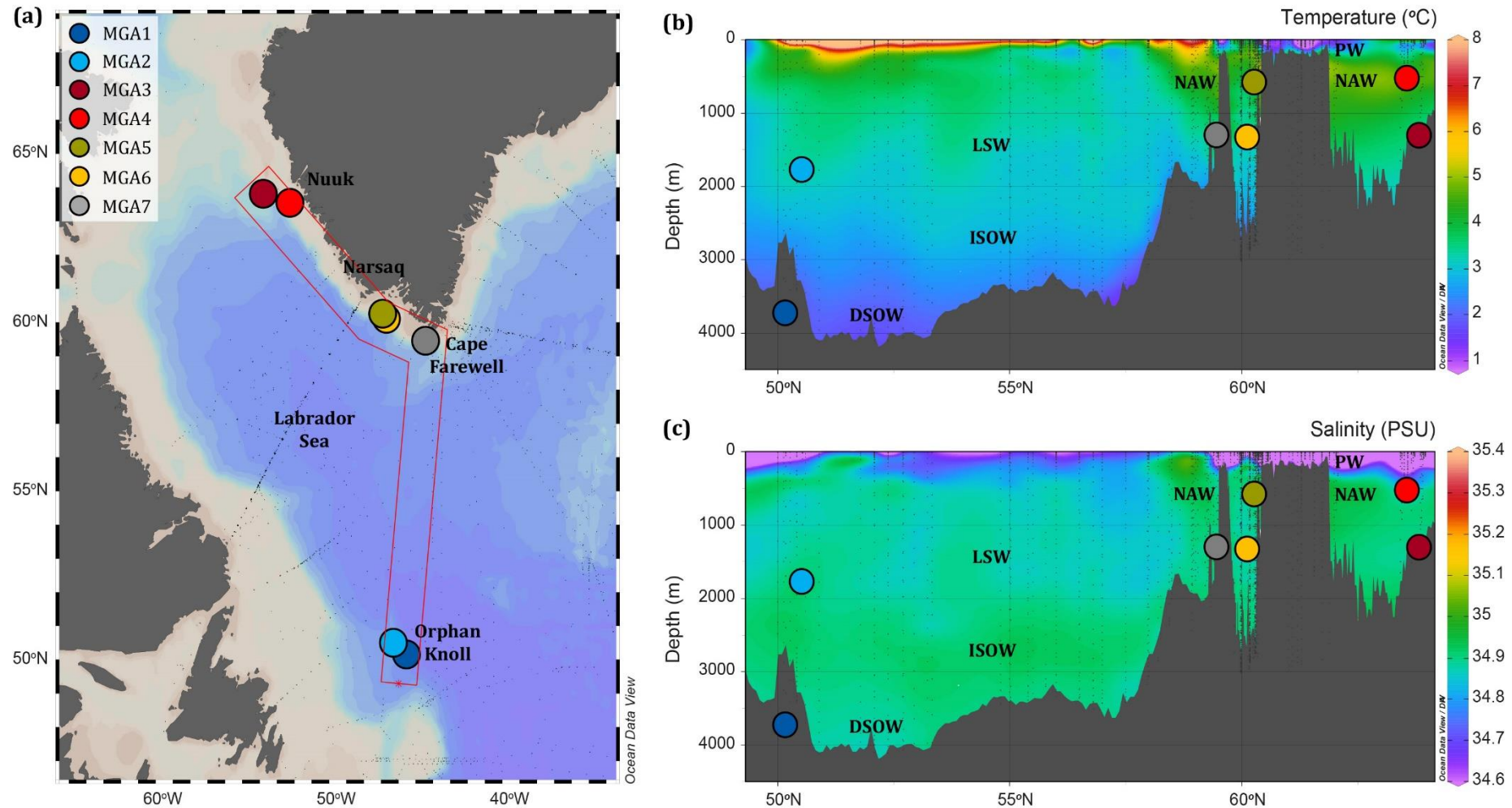
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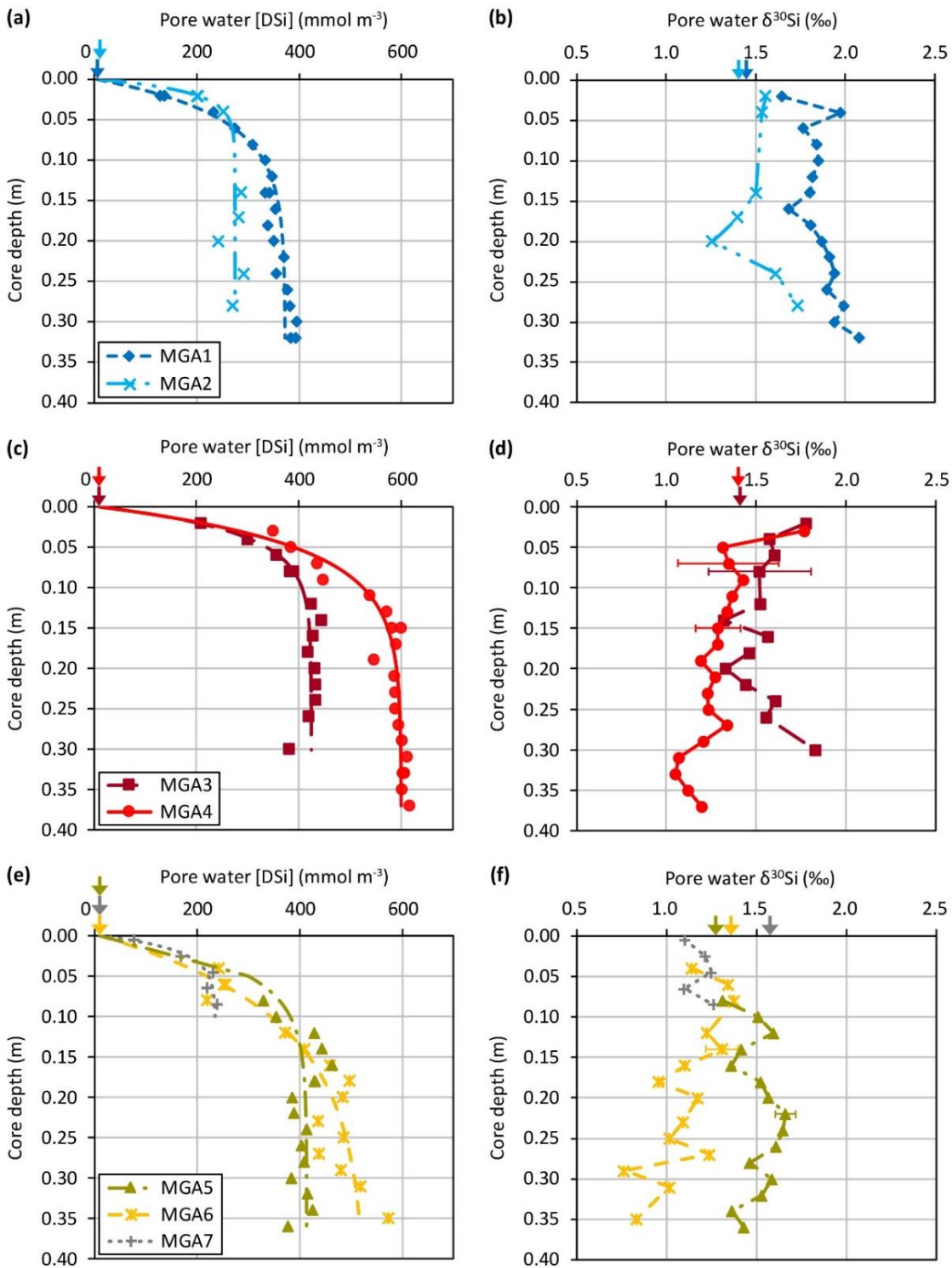
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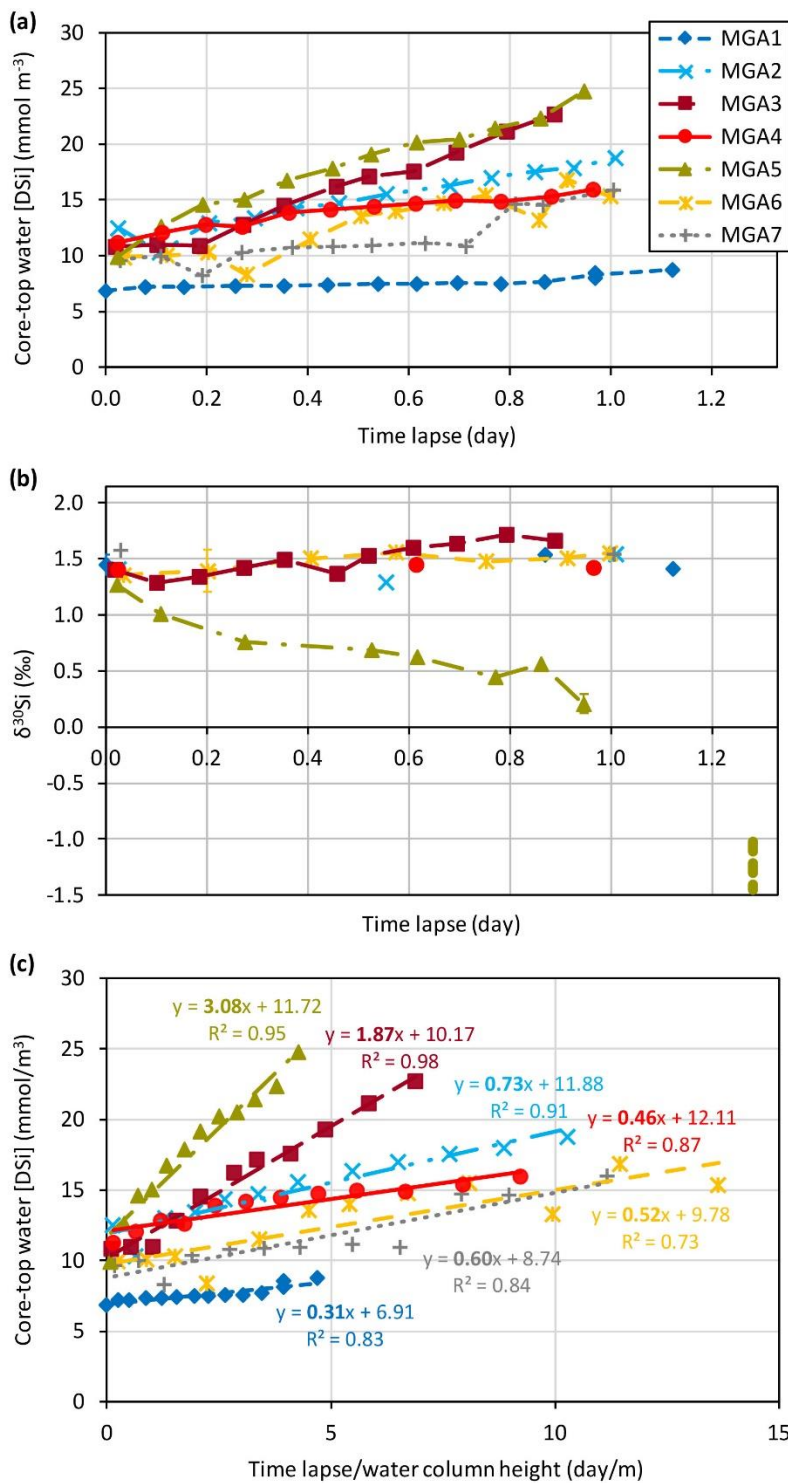
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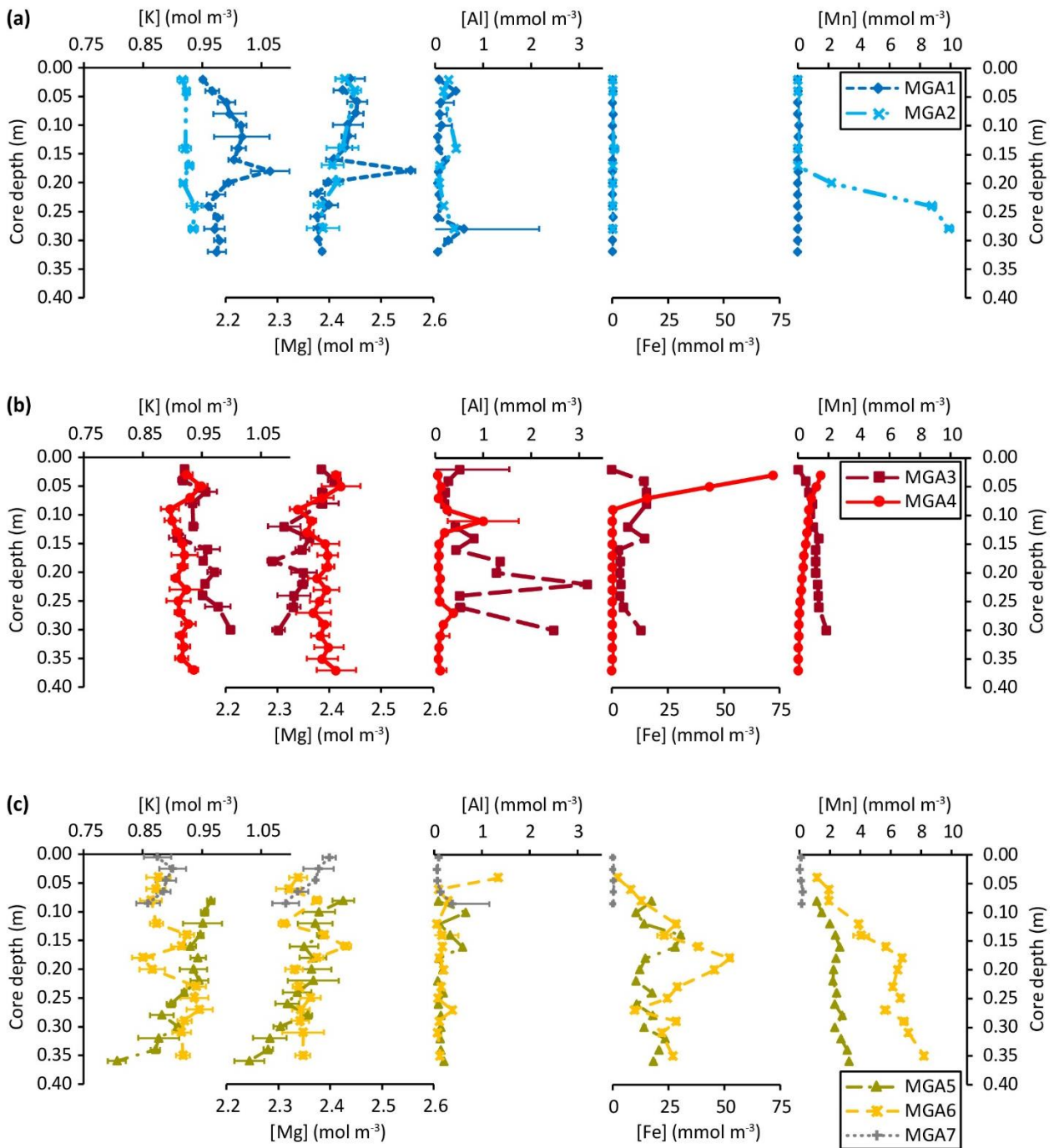
Figure 1. Locations of mega cores in this study. **(a)** Site map. Red line drawn on the map defines the boundary of the depth sections. Depth sections of **(b)** temperature and **(c)** salinity, showing the major water masses on the Greenland margin and in the Labrador Sea: Polar Water (PW), North Atlantic Water (NAW), Labrador Sea Water (LSW), Iceland-Scotland Overflow Water (ISOW), and Denmark Strait Overflow Water (DSOW). The temperature and salinity data (black dots) include new measurements from the DY081 cruise (Hendry et al., 2019b), and existing ones from the GLODAPv2 database (Olsen et al., 2016), which were interpolated in colour employing the DIVA method, an in-built function in ODV (Schlitzer, 2012). Bathymetry shown in dark grey is from GEBCO 30 arc-second grid (Weatherall et al., 2015), and sites may appear to be 'below' or 'floating above' the seafloor because they are superimposed on a representative section across the Atlantic, rather than the overlying bathymetry measured at the actual sites. The figure was generated using the ODV program (Schlitzer, 2012).



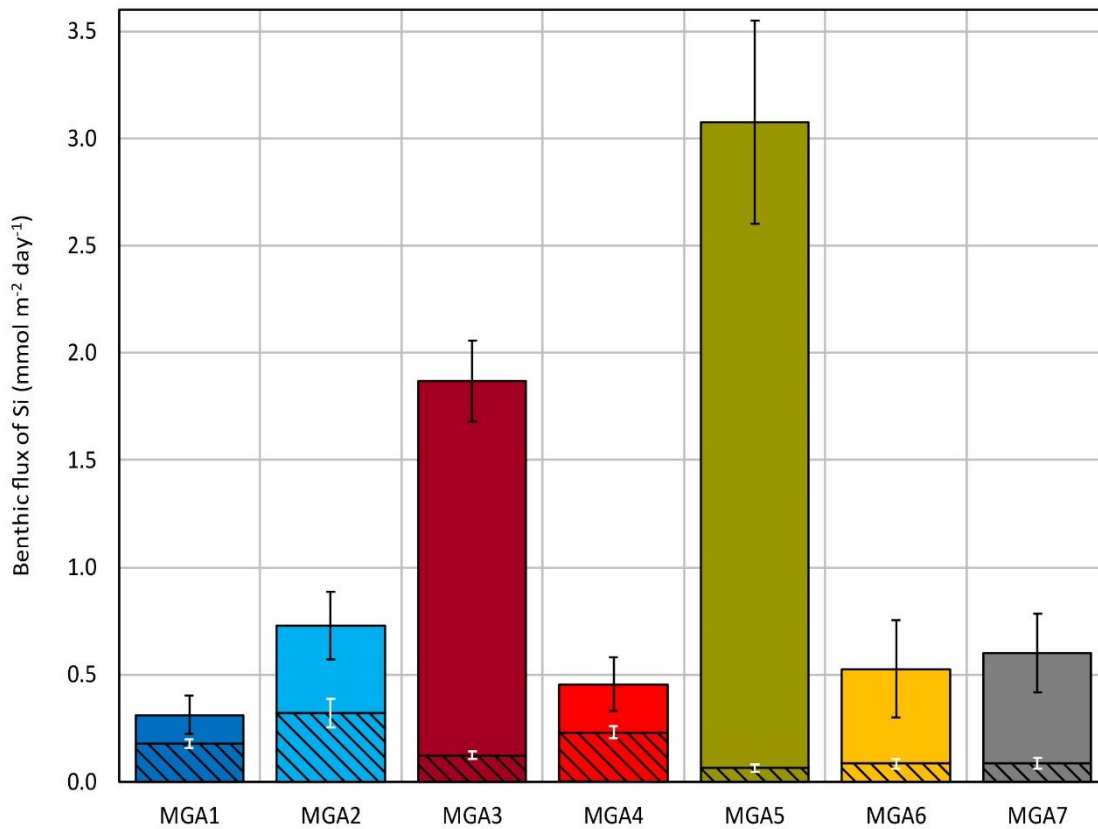
678
 679 **Figure 2.** Pore water [DSi] and $\delta^{30}\text{Si}$ results. The mega cores are grouped together based on the
 680 geographical regions: Labrador Sea MGA1 and MGA2 **(a)** [DSi] and **(b)** $\delta^{30}\text{Si}$ profiles; West Greenland margin
 681 MGA3 and MGA4 **(c)** [DSi] and **(d)** $\delta^{30}\text{Si}$ profiles; South-West Greenland margin MGA5, MGA6 and MGA7 **(e)**
 682 [DSi] and **(f)** $\delta^{30}\text{Si}$ profiles. Lines in the [DSi] plots are (least squares) exponential fitting of the data carried
 683 out using SigmaPlot (Systat Software Inc.). The arrows mark the core-top seawater [DSi] and $\delta^{30}\text{Si}$ obtained
 684 from 0.14–0.32 m height above the sediment-water interface. Horizontal error bars represent 2 SD of
 685 repeat sample $\delta^{30}\text{Si}$ measurements ($n = 2-3$) carried out on the following sample intervals: MGA3-0.08 m,
 686 MGA4-0.07 m, MGA4-0.15 m, MGA5-0.22 m, and MGA6-0.14 m. MGA7 has a very short sediment core
 687 length, and hence there is only pore water data down to ~ 0.1 m. The lack of pore water data at the top
 688 portion of MGA5 sediment core is due to a slanted core top, and hence sampling above 0.08 m core depth
 689 would mostly be extracting core-top water instead of pore water.



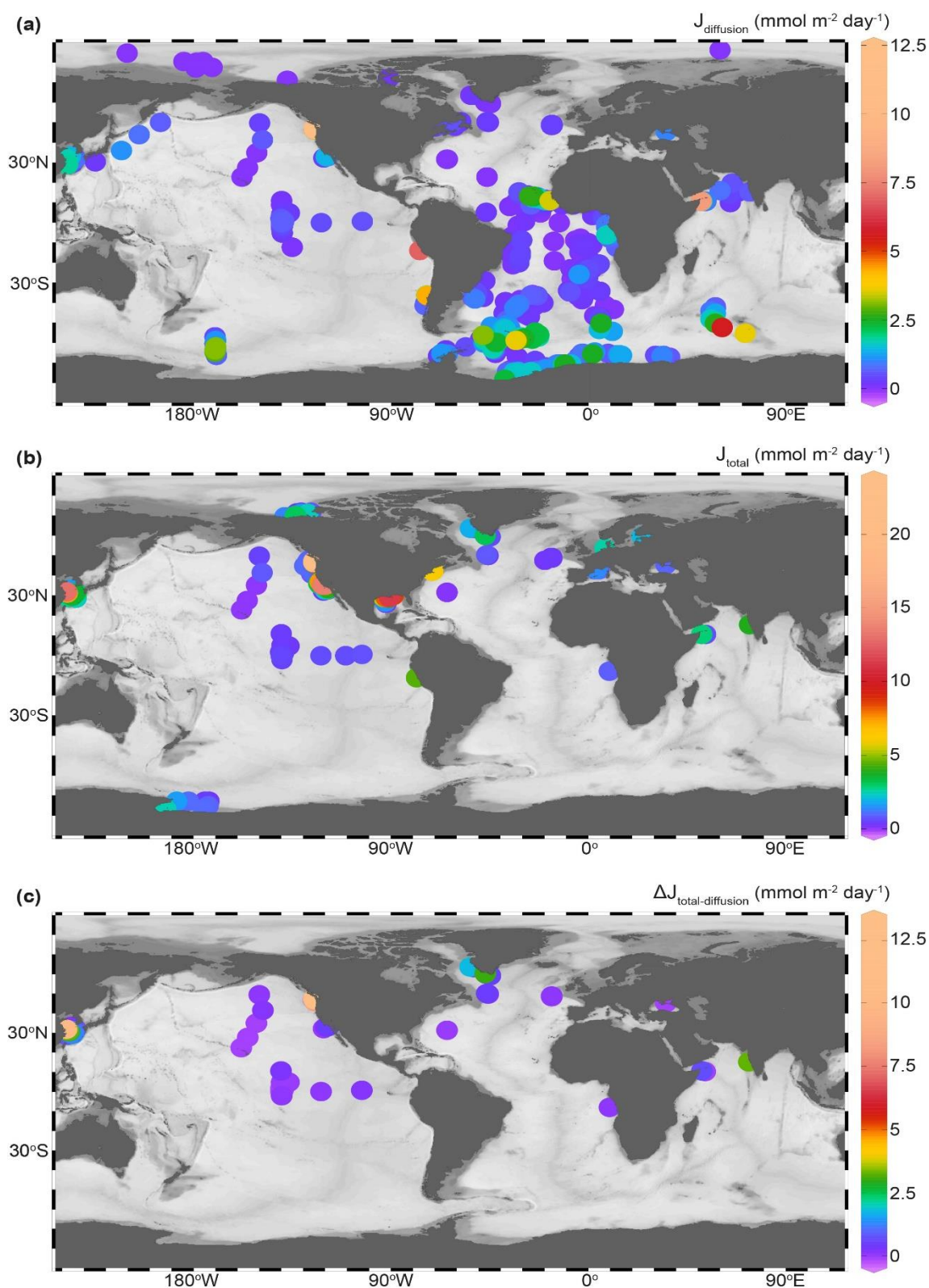
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 691 **Figure 3.** Core incubation results. **(a)** Core-top water [DSi], and **(b)** core-top water δ³⁰Si, both against the
 692 time elapsed since the beginning of incubation. Vertical error bars represent 2 SD of repeat sample δ³⁰Si
 693 measurements (n = 2–3) carried out on the following sample intervals: MGA1-0 day, MGA3-0.19 day,
 694 MGA3-0.35 day, MGA5-0.95 day, and MGA6-0.20 day. Some of the error bars are too small to be visible in
 695 the figure. Thick dashed vertical bars at the right of the plot indicate δ³⁰Si range of sponges found atop the
 696 sediment column of MGA5. **(c)** Linear regressions of core-top water [DSi] against the ratio of incubation
 697 time to water column height. The slopes of the lines (bold text) are the apparent total benthic Si fluxes in
 698 the core incubations. All the linear regressions have p-values of less than 0.05, justifying the use of a linear
 699 model to describe the relationship above.



700
 701 **Figure 4.** Pore water dissolved concentrations of major elements: [K], [Mg] and trace elements: [Al], [Fe],
 702 [Mn]. Element concentration profiles of **(a)** MGA1 and MGA2 from the Labrador Sea, **(b)** MGA3 and MGA4
 703 from West Greenland margin, **(c)** MGA5, MGA6 and MGA7 from South-West Greenland margin. Horizontal
 704 error bars represent 2 SD analytical uncertainties, some of them are too small to be visible in the figure.



705
 706 **Figure 5.** Benthic fluxes of Si at the study sites MGA1–MGA7. The entire lengths of the vertical columns
 707 represent the total benthic Si fluxes, J_{total} , measured from the core incubation experiments; while the
 708 hashed portion of the vertical columns denotes the benthic Si fluxes by molecular diffusion, $J_{diffusion}$,
 709 calculated from the pore water [DSi] profiles. The black and white error bars indicate the 95 % confidence
 710 intervals of J_{total} and $J_{diffusion}$ respectively.



711
 712 **Figure 6.** Compilation of global benthic Si flux data. **(a)** Diffusive benthic Si fluxes, $J_{\text{diffusion}}$, derived from pore
 713 water [DSi] profiles; **(b)** Apparent total benthic Si fluxes, J_{total} , measured using the in-situ benthic chamber
 714 method, or the laboratory core incubation method; **(c)** Differences between J_{total} and $J_{\text{diffusion}}$, $\Delta J_{\text{total-diffusion}}$.
 715 Data are plotted as circles with colour maps defined by the legends, and full references for the compiled
 716 data are listed in Appendix Table A.1. There are some differences in the magnitude of $J_{\text{diffusion}}$ between our
 717 compilation in plot (a), and that in (Frings, 2017), as they have carried out a reevaluation of the compiled
 718 $J_{\text{diffusion}}$ while we keep the original values presented in previous studies. However, the difference above does

719 not undermine the main observations discussed in the paper. The figure was generated using the ODV
720 program (Schlitzer, 2012).

721 **Table 1.** Study site information and sediment core description.

Core name	Site	Latitude (°N)	Longitude (°E)	Water depth (m)	Date of sampling	Basic sediment core log
DY081-MGA1	Labrador Sea	50.1592	-45.5083	3721	8 July 2017	0 – 0.4 m: greyish yellow sandy clay. Abundant foraminifera. Low bioturbation. Trace amount of very fine pebbles.
DY081-MGA2	Labrador Sea (Orphan Knoll seamount)	50.5155	-46.2790	1770	11 July 2017	Core top: green fluffy detritus. 0 – 0.15 m: dull yellowish brown muddy medium sand fining downwards. Abundant foraminifera. 0.15 – 0.38 m: yellowish brown mud. No obvious bioturbation. Small amount of fine angular pebbles.
DY081-MGA3	South West Greenland margin (off Nuuk)	63.8154	-53.7743	1301	17 July 2017	0 – 0.37 m: greyish brown muddy fine sand. Moderate bioturbation.
DY081-MGA4	South West Greenland margin (off Nuuk)	63.5530	-52.2251	519	24 July 2017	0 – 0.41 m: greyish olive mud. Low bioturbation. Strong rotten egg smell.
DY081-MGA5	South Greenland margin (off Narsaq)	60.2618	-46.8908	572	27 July 2017	Core top: diverse biology (sponges attached to coarse pebbles atop the sediment column, bivalves, annelid, shrimps). 0 – 0.10 m: grey pebbly sandy mud. Moderate bioturbation. 0.10 – 0.37 m: grey muddy clay. Low bioturbation.
DY081-MGA6	South Greenland margin (off Narsaq)	60.1160	-46.6635	1327	28 July 2017	Core top: fluffy detritus. 0 – 0.38 m: grey sandy silt. Moderate abundance of shell fragments. Low bioturbation.
DY081-MGA7	South Greenland margin (off Cape Farewell)	59.4564	-44.4151	1292	30 July 2017	Core top: green fluffy detritus, shell fragments. 0 – 0.16 m: yellowish grey sandy mud. Low bioturbation.

722

723 **Table 2.** Comparison of reference standard Si isotope composition measured in this study with published values. Measured values are long-term averages of
 724 repeat analysis of the standards over the duration of this study (September 2017–October 2018).

Reference standard	Number of replicate measurements	Measured value (‰)		Published value (‰)		Reference
		$\delta^{30}\text{Si}$	2 SD	$\delta^{30}\text{Si}$	2 SD	
Diatomite	28	+1.23	0.12	+1.26	0.20	(Reynolds et al., 2007)
LMG08 sponge	26	-3.47	0.10	-3.43	0.15	(Hendry and Robinson, 2012)
ALOHA ₁₀₀₀ seawater	10	+1.17	0.17	+1.24	0.20	(Grasse et al., 2017)

725

726 **Table 3.** List of parameters used to estimate the diffusion Si flux, $J_{\text{diffusion}}$, at the sediment-water interface. Definition: ϕ_0 – core-top sediment porosity, θ^2 –
727 tortuosity, D_m – molecular diffusion coefficient for silicic acid in free solution, C_0 – ambient core-top water [DSi], C_d – asymptotic pore water [DSi], β – an
728 expression related to the sediment depth at which pore water [DSi] reaches C_d . The uncertainty associated with $J_{\text{diffusion}}$ was calculated with standard error
729 propagation assuming Gaussian distribution, using the following formula: $2SD_{J_{\text{diffusion}}} = \left(\frac{2SD_{\phi_0}}{\phi_0} + \frac{2SD_{D_m}}{D_m} + \frac{2SD_{\theta^2}}{\theta^2} + \frac{2SD_{\beta}}{\beta} + \left(\frac{2SD_{C_d} + 2SD_{C_0}}{C_d - C_0} \right) \right) \times J_{\text{diffusion}}$

	ϕ_0 ^[i]	2 SD	θ^2 ^[ii]	2 SD	D_m (m ² day ⁻¹) ^[iii]	2 SD	C_0 (mmol m ⁻³) ^[iv]	2 SD	C_d (mmol m ⁻³) ^[v]	2 SD	β (m ⁻¹) ^[v]	2 SD
MGA1	0.806	0.003	1.431	0.007	4.02 x 10 ⁻⁵	1.6 x 10 ⁻⁶	6.82	0.27	373.0	4.9	21.5	1.3
MGA2	0.727	0.003	1.638	0.008	4.32 x 10 ⁻⁵	1.5 x 10 ⁻⁶	12.49	0.50	275.2	7.5	63.6	8.3
MGA3	0.514	0.003	2.331	0.012	4.38 x 10 ⁻⁵	1.5 x 10 ⁻⁶	10.83	0.43	424.2	5.9	31.1	2.2
MGA4	0.713	0.003	1.677	0.008	4.49 x 10 ⁻⁵	1.4 x 10 ⁻⁶	11.20	0.45	599.4	8.3	20.6	1.5
MGA5	0.395	0.003	2.858	0.015	4.53 x 10 ⁻⁵	1.4 x 10 ⁻⁶	9.88	0.40	413.8	9.8	25.2	5.8
MGA6	0.656	0.004	1.843	0.012	4.44 x 10 ⁻⁵	1.5 x 10 ⁻⁶	9.88	0.40	531.1	27.7	10.2	1.6
MGA7	0.419	0.003	2.740	0.014	4.44 x 10 ⁻⁵	1.5 x 10 ⁻⁶	9.64	0.39	235.7	11.7	56.5	11.3

730 ^[i] ϕ_0 , defined as the ratio of pore volume to total volume of sediment, was determined from weight measurement of core-top sediment sample (Schulz and Zabel,
731 2006).

732 ^[ii] θ^2 was calculated using the equation: $\theta^2 = 1 - \ln(\phi_0^2)$ (Boudreau, 1996).

733 ^[iii] D_m is dependent on temperature. Determination of D_m for the study sites were based on previous experimental study on D_m values at a range of temperature
734 (Rebreanu et al., 2008), given proximal bottom water temperatures acquired from DY081 cruise expedition.

735 ^[iv] Core-top water [DSi] measurements at the beginning of MGA1–MGA7 core incubation experiments (Fig. 3) were used to define C_0 , assuming there was little
736 change in the initial [DSi] within the heights of the core-top water columns, as the samples were taken 0.14–0.32 m above the core-top sediment.

737 ^[v] C_d and β were evaluated from Equation (3) through least squares exponential fit of the pore water [DSi] profiles (Fig. 2a, c & e) with C_0 values defined above. For
738 each core site, the exponential fit was carried out on all pore water [DSi] data (including all repeat measurements without prior averaging or weighting) using the
739 Regression Wizard function in SigmaPlot (Systat Software Inc.).

740 **Table 4.** Benthic Si flux mass balance parameters.

Core	$\frac{d(C \cdot \delta^{30}\text{Si}_{\text{core-top water}})}{d(t/h)}$ (mmol m ⁻² day ⁻¹)	J _{diffusion} (mmol m ⁻² day ⁻¹)	J _{sponge} (mmol m ⁻² day ⁻¹)	J _{residual} (mmol m ⁻² day ⁻¹)	$\delta^{30}\text{Si}_{\text{diffusion}}$ (‰)	$\delta^{30}\text{Si}_{\text{sponge}}$ (‰)	$\delta^{30}\text{Si}_{\text{residual}}$ (‰)
MGA1	0.52	0.18	-	0.13	1.65	-	1.67
MGA2	1.12	0.32	-	0.41	1.56	-	1.53
MGA3	3.29	0.12	-	1.74	1.78	-	1.76
MGA4	0.76	0.23	-	0.22	1.77	-	1.57
MGA5	-1.79	0.06	2.53	0.48 ^[i]	1.31	-1.25	2.71
MGA6	0.77	0.08	-	0.44	1.14	-	1.54
MGA7	0.86	0.09	-	0.52	1.10	-	1.47

741 ^[i] J_{residual} of MGA5 is assumed to be the average of those from proximal sites MGA6 and MGA7.