Diatom Productivity Boosts Subpolar Carbon Pump Over the Last Millennium

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Abstract

Human-induced warming is proposed to globally weaken the biological carbon 13 pump by increasing ocean stratification and by altering marine community struc-14 ture [1-3]. However, there are hints that these relationships may break down 15 in different regional environments [4]. The sediment core RAPiD-21-3K from 16 the subpolar North Atlantic provides decadal-resolution data spanning back to 17 1200 CE, offering valuable insight into changes in biological carbon export under 18 anthropogenic climate change. Sinking diatoms dominated marine carbon export, 19 and here we present a decadal-centennial-scale analysis of changes in diatom frus-20 tule silica mass and size ('silica-per-particle'). A decline in diatom silicification 21 was observed, aligning with a freshening of the Subpolar Gyre, amidst variations 22 driven by the North Atlantic Oscillation (NAO). Additionally, strongly correlated 23 records of total organic carbon and diatom export flux show a rise in diatom abun-24 dance in response to sea surface warming. We propose that human-driven changes 25

²⁶ have likely enhanced the biological pump in this region by promoting aggregate

27 formation and increasing sinking efficiency, with important implications for future

28 carbon sequestration in a warming ocean.

29 Keywords: biological carbon pump, diatoms, climate, North Atlantic Ocean

30 Main

Enhanced sinking facilitates the export of particulate organic carbon (POC) from the 31 surface ocean to the seafloor sediments to strengthen the biological carbon pump. 32 The North Atlantic accounts for 5-18% of global carbon export via this pump [5], yet 33 despite being one of the most extensively sampled ocean regions, uncertainty remains 34 about the direction of both past and future changes in its biological carbon pump 35 strength. Diatoms contribute approximately 40% of global carbon export from the 36 euphotic zone [6] and promote substantial carbon sinking in the spring phytoplankton 37 blooms of the subpolar North Atlantic. Whilst diatoms may not entirely dominate 38 these bloom assemblages [7], ungrazed diatom aggregates account for 99% of cell flux 30 at 750m depth in the Iceland Basin [8, 9].

Particulate organic carbon, in the form of photosynthetically-produced molecules within diatoms, sinks from the euphotic zone (POC export) and continues through the mesopelagic zone (POC transfer). This process persists until POC is either remineralized by zooplanktonic and prokaryotic grazers [10, 11] or sequestered in deep-ocean sediments. The opaline silica frustule of diatoms protects POC from remineralization, enabling deeper sinking and prolonged carbon storage [12]. Although there is a known correlation between opal and POC fluxes to the deep sea [13], not all diatoms contribute equally to POC sinking. Diatoms with thicker, more silicified cell walls tend to sink faster and offer greater mechanical resistance, enhancing their export potential

⁵⁰ [6]. However, individual diatoms are highly labile, making the aggregation of multiple ⁵¹ diatoms or faecal repackaging the most efficient ways to resist remineralization and ⁵² transfer POC to the seafloor [14, 15]. Additionally, siliceous zooplankton like Radi-⁵³ olaria have soft-bodied POC components, which can become trapped in aggregates ⁵⁴ or form faecal pellets that contribute to the sinking POC flux [16]. Genetic analyses ⁵⁵ reveal that diatoms (15.4%) and rhizarians, including Radiolaria (26.9%) dominate ⁵⁶ the plankton exported to and accumulating on the global seafloor [17].

Subpolar North Atlantic diatom blooms are primarily limited by silicate concentra-57 tions and, at times, by iron [18, 19]. Globally, rising sea surface temperature (SST) 58 and increased stratification could reduce the upwelling of these nutrients, decreasing 50 phytoplankton productivity while accelerating grazer respiration rates. This combi-60 nation is expected to shallow the remineralization depth and weaken the biological 61 carbon pump under future climate warming [1-3]. However, recent increases in SST 62 and changes in ocean mixing have enhanced the biological uptake of atmospheric CO_2 63 and boosted diatom biomass in the subpolar North Atlantic [20, 21]. As a result, the 64 subpolar North Atlantic may counter the global trend, potentially strengthening its 65 biological carbon pump in a warmer climate. 66

This study analyzed a sediment core from the subpolar North Atlantic to evaluate 67 decadal- to centennial-scale variability in the local biological carbon pump strength 68 over the past ~ 800 years (1213 to 2001 CE). We measured the area, thickness, and 69 silica masses of individual Coscinodiscus sp. [22] diatom frustules and Hexacontium 70 sp. [23] radiolarian tests within their typical size fraction (125-150 μ m) [24], as Cos-71 cinodiscus was likely the primary exporter of POC to the seafloor at this Reykjanes 72 Ridge site. Downcore X-ray fluorescence was used to estimate the sedimentary flux of 73 diatoms and total organic carbon from the calibrated mass fluxes of silica and bromine 74 respectively [25–27]. The sediment core provided a means to combine export and 75

- ⁷⁶ transfer efficiencies while assuming permanent POC storage in the sediments, offer-
- π $\,$ ing a first-order representation of the biological carbon pump strength. This approach
- ⁷⁸ allowed us to examine how changes in diatom morphology and abundance influenced
- 79 the strength of the subpolar North Atlantic biological carbon pump over the past
- $_{\rm so}~$ ${\sim}800$ years and to identify the climatic drivers behind these variations.

⁸¹ Silica-per-Particle Decline Reflected in Diatom

82 Geometries





(a) Silica mass-per-diatom particle including replicates and error envelope of 7.33%. (b) Silica mass-per-radiolarian particle including replicates, outliers (see Methods) and error envelope of 9.23%. (c, d) SEM-measured areas (green) and thicknesses (light blue) of individual frustules (open circles) and sample averages (green/light blue line) with an error envelope corresponding to the standard error. All datasets include mean (dashed gray line) and linear trend (black solid line). Vertical grey bars represent the excursion period 1934–1971 CE observed in all datasets. Light and dark bars represent positive and negative excursions respectively; note the inversion in (d).

We developed a new methodology using inductively coupled plasma mass-83 spectrometry (see Methods) to measure changes in silica mass in individual Coscin-84 odiscus sp. [22] diatom frustules and Hexacontium sp. [23] radiolarian tests, referred 85 to as "silica-per-particle". Particles were selected from the 125-150 µm fraction to con-86 trol for size variability and assess silicification intensity within individual specimens. 87 Both records showed a declining trend over the 788-year period (Fig. 1a,b). Linear 88 trendlines indicated an overall decrease in silica-per-diatom by approximately 0.35 ngper decade (p < 0.0001) and a more gradual reduction in silica-per-radiolarian by 0.26 90 ng per decade (p=0.0051). These calculations excluded the 1934–1971 CE excursion 91 period (Fig. 1), which coincided with a significant atmospheric pressure anomaly, as 92 discussed later. 93

The silica-per-diatom values fluctuated by 53.7 ng, ranging from 34.4 ng to 88.1 ng, 94 with a mean of 65.5 ng and a variability of $\pm 41\%$. In comparison, the silica-per-95 radiolarian values had a broader range of 76.3 ng (56.5 ng to 132.7 ng) but showed lower 96 proportional variability at $\pm 29.4\%$ around a higher mean of 77.8 ng. Decadal-scale 97 variability was more pronounced in silica-per-radiolarian than in silica-per-diatom. 98 Notably, periods of significant variability overlapped in time, with low-amplitude fluc-99 tuations occurring between approximately 1614 and 1922 CE and high-amplitude 100 variability observed in the earlier and later segments of the record. These data did not 101 show any trend deviations attributable to anthropogenic forcing (Supplementary Fig. 102 1) or evidence of sustained deep current sorting (Supplementary Fig. 2). 103

¹⁰⁴ Using scanning electron microscopy (SEM), we measured diatom frustule area, thick-¹⁰⁵ ness, and porosity to determine how changes in silica mass-per-diatom translated into ¹⁰⁶ frustule geometry (Fig. 1c,d). A linear trendline revealed that frustule area declined by ¹⁰⁷ 4.13 μ m² per year (*p*=0.0090), equating to a 1.6% decrease per century–comparable to ¹⁰⁸ the 5.3% per century decline in silica-per-diatom. Frustule area showed a significant

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¹⁰⁹ positive correlation with silica-per-diatom (p=0.0033) (Supplementary Fig. 2a) and ¹¹⁰ varied by 16,000 µm² (min=17,300 µm², max=33,300 µm²) around a mean of 25,600 ¹¹¹ µm².

Frustule thickness, with a mean of 4.40 µm, varied by 2.93 µm (min=2.87 µm, 112 max=5.81 µm) but showed no clear trend over time. Detrended silica-per-diatom val-113 ues mirrored mean frustule thickness across the x-axis, with the two exhibiting a 114 significant negative correlation (p=0.0001, Supplementary Fig. 3c), indicating that 115 lighter frustules were thicker on decadal timescales. Maximum and minimum Feret's 116 Diameters followed a pattern similar to frustule area (Supplementary Fig. 3d). While 117 porosity percentage appeared stable across the record (Supplementary Fig. 3b), limited 118 sample resolution for well-defined areolae (pores) [28] precluded detailed interpretation 119 of these data (Supplementary Fig. 7a-f). 120

The strong correlation between silica-per-diatom and frustule area indicates that, over 121 centennial timescales, the long-term decline in silica-per-diatom was primarily driven 122 by reductions in frustule area-and consequently diatom size-even within our size-123 restricted sample set. The parallel patterns of silica-per-particle variability observed 124 in both diatoms and Radiolaria attests that these trends extended across multiple 125 components of the siliceous plankton assemblage. In contrast, the absence of a clear 126 trend and the narrower variability in frustule thickness suggest that thickness changes 127 did not play a significant role in the long-term silica-per-diatom decline. However, 128 the observed decadal-scale anticorrelation between frustule thickness and silica-per-129 particle hints at an inverse relationship operating on shorter timescales. 130

¹³¹ Climate Forcings as Driving Mechanisms

Subpolar Gyre Upwelling Strength Governs Diatom Size and Silica Mass

Given the reductions in cellular silica in diatoms under silicate limitation in Harrison 134 et al. [29] and Paasche [30], it is reasonable to assume that the primary factor influ-135 encing silica mass content in diatom frustules is the concentration of silicate in the 136 surrounding surface water. Diatoms from core RAPiD-21-3K are deposited from the 137 waters of the northern limb of the North Atlantic Subpolar Gyre (SPG), which are fed 138 by the cyclonic circulation of the Subpolar Front and the North Atlantic Current in 139 the Iceland Basin (Fig. 2) [31]. The surface silicate supply in the SPG is governed by 140 Ekman suction and the upwelling of recycled silica, which has dissolved into silicate at 141 depth [32]. Increased wind-stress strengthens upwelling in a stronger SPG, boosting 142 the supply of nutrients from the interior ocean reservoir, beneath the mixed layer, to 143 the depleted surface waters [33]. 144



Fig. 2 The expansion and contraction of the Subpolar Gyre drives Ekman upwelling. Schematic map of major surface (solid arrows) and deep (black dotted arrows) currents in the North Atlantic, near to the site of core RAPiD-21-3K (orange circle). Red arrows indicate currents under a positive NAO and expanded SPG, yellow arrows indicate those under a negative NAO and contracted SPG, and orange arrows indicate those present under both states. Currents affecting the upwelling of the Subpolar Gyre are emboldened. RR, Reykjanes Ridge; NAC, North Atlantic Current. Adapted from Sarafanov (2009) [34].

To explore the cause of the long-term decline in silica-per-diatom over the millennium, 145 we compared the raw silica-per-diatom data with modeled simulations of spatially-146 averaged SPG strength (Past1000-R1, -R2, and -R3) from Moreno-Chamarro et al. 147 [35] (Fig. 3d,e). These simulations, which span the past 1000 years, incorporate varia-148 tions in atmospheric aerosols, greenhouse gas concentrations, and solar parameters to 149 produce an SPG strength index based on the spatially averaged barotropic streamfunc-150 tion. Two of the simulations showed a gradual SPG weakening of 0.10 Sv per century, 151 whilst the third simulation (Past1000-R3) displayed a rapid shift from a strong to 152

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weak SPG around 1600 CE, with a 0.72 Sv drop. We applied a change-point algo-153 rithm (see Methods) to detect abrupt shifts in both the raw silica-per-diatom record 154 and Past1000-R3 for our core-site grid square (Fig. 3d,e). In Past1000-R3, the SPG 155 weakening was marked by an abrupt shift in 1602 CE, with a larger 1.13 Sv change 156 in this region. The algorithm identified a shift between two stable silica-per-diatom 157 regimes in 1633 CE, which appeared to be more gradual than the SPG weakening, 158 starting between 1595–1614 CE and ending around 1673 CE. Abrupt shifts in 1934 159 and 1963 CE bookend the negative NAO-driven excursion in Fig. 1, emphasizing its 160 exceptional nature. 161



Fig. 3 The NAO and gyre strength as the decadal- and centennial-scale drivers in silica mass-per-particle.

(a) Proxy-reconstructed (red) from Ortega et al. [36] and observed (orange) from NOAA [37] North Atlantic Oscillation (NAO) index, with Savitzky-Golay filtering (see Methods) applied. (b) Detrended silica-per-particle with detrended mean (gray dashed line). (c) Two-tailed moving Pearson's correlation over a \pm 36-yr window to test for a correlation between the NAO index and detrended silica-mass-per-diatom particle. Pearson's r was plotted against age to highlight periods of strong correlation (p<0.01, green), good correlation (p<0.05, yellow) and moderate correlation (p<0.1, red), as given in the colorbar. These periods are also shown as vertical regions in (a) and (b), with grey regions reflecting periods of anticorrelation. (d) Barometric streamfunction reflecting Subpolar Gyre strength at 57°N, 333°E for 1200–1850 CE from simulation Past1000-R3 of Moreno-Chamarro et al. [35] with decadal moving average. The abrupt change in signal (vertical dashed line). The y-axis is inverted to indicate the gyre strength decline despite a negative (cyclonic) streamfunction. (e) Silica-per-diatom particle with abrupt signal changes (vertical dashed lines) at 1633, 1934, and 1963 CE. Signal period means (horizontal gray dashed line) and the signal change from (d)(vertical dotted line) are also shown, and the first region of NAO/silica-per-diatom anticorrelation from (c) is overlain.

The shift in silica-per-diatom around 1600 CE may have shared the same cause as the 162 relatively coincident SPG weakening, which Moreno-Chamarro et al. [35] attributed 163 to surface ocean freshening in the western subpolar North Atlantic. They proposed 164 that increased export of sea ice from the Arctic Ocean and Nordic Seas into the 165 Labrador Sea melted, causing sea-surface salinity to drop by 0.20 psu. This weakened 166 the zonal density gradient between the western and eastern SPG, leading to SPG 167 weakening. Reduced advection of saline waters and curbed deepwater mixing delayed 168 the recovery from this shift until after 1640 CE, a prolonged decline reflected in our 169 silica-per-diatom record. 170

Over multidecadal timescales, the wind-stress curl on the SPG is primarily influ-171 enced by sustained forcing of the North Atlantic Oscillation (NAO) [38]. The NAO 172 is quantified by the NAO index, wherein an index amplification (+NAO) reflects 173 the strengthening of westerly winds, which strengthen and expand the SPG (Fig. 2) 174 [39, 40], leading to enhanced silicate upwelling and a greater supply to the surface 175 [18]. The relation between short-term, multi-decadal variability in silica-per-diatom at 176 our core site and NAO-driven variability in surface silicate concentration was tested 177 by applying a running correlation between a multi-proxy NAO index reconstruction 178 for the past millennium [36]) and detrended silica-per-diatom (Fig. 3a,b). A running 179 right-tailed Pearson's Correlation was applied over a ± 36 -year window and correlation 180 was plotted at the 10%, 5% and 1% significance levels (Fig. 3c). Detrended silica-181 per-diatom was positively correlated with the reconstructed NAO index at the 5%182 significance level for 72.5% (584 years) of the record. A moving correlation was also 183 tested against the reconstructed Atlantic Multidecadal Oscillation (AMO) Index of 184 Michel et al. [41], at a range of window lengths, but the maximum correlation was both 185 weaker and considerably less sustained (31.6%, 249 years) (Supplementary Fig. 4). 186

From 1934 to 1971 CE, the pronounced excursion was marked by an extreme mini-187 mum in silica per diatom in 1954. This deviation was negative in all records in Fig. 1, 188 except for frustule thickness. This silica-per-diatom excursion appears to be an excep-189 tional event within the record and was strongly correlated with a similar low in the 190 NAO index, with Pearson's r not dropping below 0.75 for this interval (Fig. 3c). This 191 indicates a reduced supply of silicate and possibly other nutrients to the surface dur-192 ing this period, likely caused by a restricted gyre extent, which significantly hindered 193 frustule growth. In contrast, Fig. 1 reveals that frustule thickness increased during this 194 period. This aligns with the observations of Wilken et al. [42], who found that iron 195 limitation raises the cellular silica content in diatoms, suggesting they develop thicker 196 and possibly mechanically stronger frustules under such conditions. 197

The abrupt signal shifts in both the SPG strength index of Moreno-Chamarro et al. [35] and silica-per-diatom (Fig. 3d,e) coincide with the most prominent period of anticorrelation between detrended silica-per-diatom and the NAO index ('Anti.1' in Fig. 3a,b,e). Perhaps the freshening outcompetes the NAO as the governor of SPG strength during this interval, explaining the observed anticorrelation.

In summary, the centennial-scale decline in silica-per-diatom, driven by a sudden freshening of the SPG, was overlain by short-term, multi-decadal shifts in silicate availability driven by NAO variability. During periods of a restricted SPG, smaller, thicker diatoms dominated, while larger, thinner diatoms thrived under strong westerly winds and enhanced upwelling. Overall, the strength of the SPG and its upwelling-driven by both NAO variability and zonal density gradients-plays a crucial role in regulating silica mass and diatom frustule size on both multi-decadal and centennial timescales.

²¹⁰ Sea-Surface Temperature Controls Diatom Abundance

To complement the silica-per-particle measurements from individual diatom frustules. 211 we calculated the sedimentary flux of frustules, providing a centennial-scale record 212 of the number of diatoms exported to the seafloor. By comparing silica-per-diatom, 213 frustule area, frustule thickness, and diatom abundance, we identified the primary 214 driver of regional biological pump strength. X-ray fluorescence (XRF) scanning was 215 applied to core RAPiD-21-3K to measure silicon activity, which was calibrated into 216 weight percent [43, 44]. These data, combined with the downcore dry bulk density 217 and sedimentation rate, was used to estimate the sedimentary bulk silica mass flux at 218 yearly resolution (see Methods, Supplementary Fig. 8). The total silica mass flux was 219 then divided by silica-per-diatom to estimate the diatom flux to the sediment at an 220 average sampling resolution of ~ 8 yrs (Fig. 4a). 221

The assumption that silica mass flux is primarily driven by the studied *Coscinodiscus* 222 genus, despite it being just one among a diverse plankton assemblage, is reasonable 223 given its likely dominant role in contributing to sinking particulate organic carbon 224 (POC) at this site. Whilst sedimentary silica mass may also reflect inputs from various 225 diatom, radiolarian, and sponge species of different sizes, ungrazed diatom aggregates 226 account for 99% of the exported cell flux at depth in this Reykjanes Ridge region [9]. 22 Within the diatom assemblage deposited in this core, Miettinen et al. [45] identified 228 10 genera that each contributed to more than 1% of the total community (Supple-229 mentary Fig. 5a). Although Coscinodiscus constituted only a small but stable fraction 230 of the assemblage (mean = 2.4%), its median biovolume, as reported by HELCOM 231 for the Baltic Sea [24], is up to 21.6 times larger than that of the most abundant 232 Thalassiosira species in this core (mean = 21.4%) (Supplementary Fig. 5b). This sug-233 gests that *Coscinodiscus* likely contributed disproportionately more organic carbon 234 and silica to the sediment compared to other species. Even so, the similar silica-per-235 particle profile observed for *Hexacontium* Radiolaria and their shared sedimentation 236

rate variability indicate that other components of the silicifying plankton community,
such as additional diatom or radiolarian species, likely exhibit comparable patterns of
sedimentary flux throughout the record.

We compared our diatom flux record to several proxy reconstructions of sea-240 surface temperature (SST) in the subpolar North Atlantic. These included Northern 241 Hemisphere multi-proxy composites [46, 47] (Fig. 4c,d), the percentage of cold-water-242 dwelling Neogloboquadrina pachyderma (sinistral) planktonic foraminifera in sediment 243 core RAPiD-35-25B South of Greenland [48] (Fig. 4e), and Mg/Ca SST calibrations 244 from the planktonic foraminifer *Globigerina bulloides* in the same core [49] (Fig. 4f). 245 Each of these reconstructions exhibited significant linear correlations with diatom flux 246 across their respective intervals (p < 0.0093). Shared structural features between the 247 diatom flux and SST proxies included local maxima during a distinct warm period 248 between 1300 and 1500 CE (later than the Medieval Warm Period, 950–1250 CE) and 249 a post-1850 increase towards present-day values. 250

The observed increase in diatom cell concentration can be attributed to a higher divi-251 sion rate in response to rising SSTs [50]. The diatom flux record, derived from the 252 combined contributions of sedimentary silica mass, sedimentation rate, dry bulk den-253 sity, and silica-per-diatom, does not fully capture features from the silica-per-particle 254 record, such as the abrupt weakening around ~ 1600 CE or the 1934–1971 excur-255 sion. Instead, other patterns emerge, including the post-1850 anthropogenic increase 256 in diatom abundance and the local minimum in 1971. Edwards et al. [21] noted a 257 similar decline in total diatom abundance in the 1960s–1970s, which they linked to 258 hydro-climatic instability caused by low temperature and salinity anomalies [51], col-259 lectively termed the 'Great Salinity Anomaly' [52]. Following this period, Edwards 260 et al. [21] reported a 50-yr rise in diatom populations in this region of the subpolar 261

- $_{\rm 262}$ $\,$ North Atlantic, significantly correlated with SST. These findings underscore SST as
- $_{\rm 263}$ $\,$ the dominant driver of diatom export flux in this region.



Fig. 4 More numerous, smaller diatoms correlated with increasing sedimentary total organic carbon and sea-surface temperature.

(a) Diatom abundance from the bulk sedimentary silica mass flux divided by silica-per-diatom. (b) Bromine XRF counts calibrated into Br mass flux as a proxy for sedimentary total organic carbon and significant positive Spearman's Rank correlation with diatom abundance. (c-f) Sea-surface temperature proxy reconstructions and their ~50-yr moving averages, and significant Spearman's Rank correlations with sedimentary diatom flux from: Hegerl et al. (2007), Mann et al. (2008), Moffa-Sánchez et al. (2014a) and Moffa-Sánchez et al. (2014b) [46–49]. All records show their mean (gray dashed line) and their linear trend (black solid line).

²⁶⁴ Implications for Biological Carbon Export

To estimate total organic carbon (TOC) in the sediments, we measured bromine activ-265 ity using X-ray fluorescence scanning and calibrated it into a downcore mass flux 266 (Fig. 4b). Bromine in sediments is strongly correlated with marine-derived organic 267 carbon [25-27], making it a reliable proxy for exported particulate organic carbon 268 (POC) reaching the seafloor. We assumed that sinking POC is primarily driven by 26 diatoms. Although some regions exhibited decoupling, the TOC profile closely mir-270 rored the diatom flux, with a strong, significant positive correlation identified via linear 271 Spearman's Rank analysis (p < 0.0001). Like the diatom flux, the POC flux displayed 272 a post-1850 CE increase towards the modern but also recorded a sharp, temporary 273 decline during the Great Salinity Anomaly [52], reaching a local minimum in 1974 274 CE. These findings suggest diatom abundance primarily controlled POC flux to the 275 sediments, which was, in-turn, regulated by SST. 276

Ungrazed diatom aggregate formation, driven by the frequency of cell collisions [53], 277 depends on diatom abundance and thus has varied throughout this record in response 278 to changing SSTs. Higher collision rates lead to larger and more numerous aggre-279 gates, resulting in a nearly linear increase in their sinking velocity [54, 55]. Elevated 280 temperatures also enhance the production of transparent exopolymer particles by 281 Coscinodiscus, improving adhesion within ungrazed aggregates and increasing the 282 proportion of POC they contain [53, 56]. However, these effects must outweigh any 283 reductions in diatom size or the accelerated growth of remineralizing bacteria [57]. 284 Notably, SST does not directly affect the sinking velocity of ungrazed aggregates by 285 altering seawater density [54]. On shorter timescales, increases in frustule thickness 286 may have improved POC resistance to grazers and enhanced its transfer efficiency through the water column [50], though this effect might be masked by changes in 288 diatom flux. 289

Future diatom-driven carbon pumping is likely to track projected anthropogenic SST 290 increases [58]. Whilst the biological pump may continue to strengthen over the coming 291 decades, a threshold may be reached where diatom abundance, total organic carbon, 292 and SST no longer correlate. Although rising SSTs have enhanced diatom productiv-293 ity in this upwelling gyre system, upper-ocean respiration rates accelerate faster than 294 photosynthesis [59]. At some tipping-point, microbial remineralization of sinking POC 295 could outpace photosynthetic carbon fixation by diatoms [60], unless diatoms adapt 296 physiologically to warmer conditions [61]. Moreover, over the last millennium, diatom 297 frustules have become smaller and lighter. If Subpolar Gyre freshening persists, fur-298 ther size reductions could hinder ungrazed diatom aggregation [53], diminishing their 299 sinking efficiency and, consequently, the biological carbon pump's effectiveness. 300

This research challenges the prevailing notion that a warming climate will inevitably 301 weaken the biological carbon pump [1-3], particularly in the subpolar North Atlantic. 302 Our findings reveal that wind- and density-driven silicate upwelling enhances diatom 303 silicification by increasing their frustule area, whilst silicate depletion results in smaller 304 but thicker frustules. When it comes to driving POC export, the sheer abundance 305 of diatoms settling into the sediments proves far more influential than their size, 306 thickness, or silica mass. This diatom flux strongly correlated with SST variability 307 and sedimentary organic carbon, underscoring the crucial role of warmer SSTs in 308 promoting effective POC sequestration in the sediments. Since the mid-19th Century, 309 rising anthropogenic SSTs have significantly boosted diatom flux and sedimentary 310 organic carbon in this region. Any assessment of the recent and future dynamics of the 311 global biological carbon pump must account for these regional shifts in temperature 312 and nutrient supply, alongside the ongoing trend of enhanced carbon export to the 313 deep ocean and sediments in the subpolar North Atlantic. 314

315 Methods

316 Material

The sediment core RAPiD-21-3K was collected in 2004 during the RRS Charles Dar-317 win's cruise CD159, funded by the UK NERC RAPiD Climate Change program. The 318 core was extracted from the Gardar Drift, on the eastern side of the Reykjanes Ridge 319 (57°27.09'N, 27°54.53'W) in the subpolar North Atlantic, south-west of Iceland in 320 2630m water depth. This site is located within the northern limb of the Subpolar Gyre, 321 along the southwestward-flowing East Reykjanes Ridge Current, which is fed by the 322 cyclonic circulation of the Subpolar Front and the North Atlantic Current in the Ice-323 land Basin [31]. Sedimentation rates are enhanced by the Iceland-Scotland Overflow 324 Water and its underlying bathymetry [62]. RAPiD-21-3K is a 15x15cm rectangular 325 kasten-core, taken in conjunction with box-core RAPiD-21-12B, to form a compos-326 ite record from the same sample site. The core is housed in the School of Earth and 327 Environmental Sciences at Cardiff University. 328

329 Silica-per-Particle

330 Sampling Strategy

Sampling of the 3.5m/2,800yr core was biased towards the recent $\sim 230yrs$ to test for anthropogenic trends against a background of more ancient sampling. After examination of the age-model of Sicre et al. [63], a constant sampling interval was proposed, as variable sedimentation rates naturally biased sample resolution towards the recent.

The uppermost one metre of core was sampled every two centimetres, beginning at 0.5cm and ending at 98.5cm depth. This gave a total of 50 samples, with temporal resolution ranging from 12.39yrs to 19.79yrs.

³³⁸ Preparation and Chemical Cleaning

The material was treated by chemical and physical cleaning adapted from Miettinen et al. [45] to remove all organic material and clays to isolate the siliceous shells. Wet samples in plastic sample bags were dried in an oven at 50°C overnight, then left to cool and weighed to four decimal places.

A buffer solution was made of 300 mL 30% hydrogen peroxide (H₂O₂), 600 mL deionised 343 water and 23mL of 0.1M NaOH, to resist changes in pH under the effervescence of 344 CO_2 during the oxidation of organic material. 75mL of this solution was added to each 345 dry sample in a borosilicate beaker (250mL, Pyrex), partially sealed with parafilm to 346 allow gas escape while avoiding material loss. In samples anomalously rich in organics, 347 H_2O_2 was used up rapidly, so up to 175mL additional buffer solution was added until 348 the reaction proceeded. Beakers were shaken overnight at 100rpm, before 0.2M sodium 349 metabisulfite (NaHSO₃, a reducing agent) was added until the effervescence from the 350 organic oxidation ceased. 351

Samples were wet sieved ($63 \mu m$, Endecotts), in tap water to maintain the saturation 352 state of SiO_2 . The fine fraction was stored, and the coarse fraction was transferred 353 to borosilicate beakers (250mL, Pyrex) with 50mL 2% 'Calgon' solution, containing 354 the active ingredients sodium hexametaphosphate $(Na_6([PO_3]_6))$ and sodium citrate 355 $(Na_x C_6 H(_{8-x})O_7)$, to dissolve the clay infillings of the siliceous shells, for 15 min-356 utes. Beakers were sonicated in an ultrasonic bath for three seconds to loosen the 357 clay material. Samples were again wet sieved into two size fractions (63 μ m and 125 358 μ m, Endecotts) using tap water. The 63-125 μ m fraction was stored, and the coarse 359 fraction was vacuum-filtered through a polycarbonate membrane (41 µm, Whatman), 360 which was placed into a plastic petri-dish (60mm, Fisherbrand) and dried in an oven 361 overnight at 50°C. The dried samples then consisted only of cleaned biomineralized 362 particles and were stored individually for microfossil separation. 363

This procedure was applied in batches of 5-10 samples, beginning at the oldest (sample 50) and ending at the youngest (sample 1). This ensured that the prioritised anthropogenic samples were cleaned most efficiently under a better-practiced method.

³⁶⁷ Microfossil Separation

The dried, coarse fraction (>125 µm) samples were dry sieved (150 µm, Endecotts) and observed under a stereo-zoom light microscope (Leica MZ 95). *Coscinodiscus* and *Hexacontium* were identified in great abundances in an initial examination of samples 50, 33 and 5 to confirm their appropriacy for use in this investigation.

60 Coscinodiscus frustules and 40 Hexacontium tests were individually picked from 372 the 125-150 µm size fraction for each sample using a single-haired paintbrush and 373 transferred to micropaleontology slides. A replicate was taken for approximately every 374 10th sample, depending on material abundance, beginning at sample 45 and ending 375 at sample 6. Fractures, dissolution holes of any size, frustules with pleural bands [28] 376 still in place, and tests with too few, too many or broken spines were strictly avoided 377 in the picked microfossils to ensure the validity of the silica-per-particle measurement 378 (Supplementary Fig. 6). 379

380 Mass Spectrometry Analysis

The following work was performed under a laminar-flow hood in a metal-free clean laboratory to preclude external contamination of silica from our results. Herein, 'samples' refers to both the diatomaceous and radiolarian portions of each sediment sample.

Frustules and tests were individually transferred via a single-haired paintbrush into 0.5mL 1.0M potassium hydroxide solution (KOH) in sealable plastic vials (0.5mL, Eppendorf) under a stereo-zoom light microscope (Leica MZ 95). Plastic vials were used to prevent silica contamination from borosilicate dissolution. Emplaced particles were counted using a desktop tally-counter to account for any losses during transfer.

The vials were sealed, and samples left to dissolve for a minimum of 60 hours. Vials 389 were hand-shaken and examined under a light microscope to ensure complete disso-390 lution. 0.45mL of each solution were pipetted into plastic centrifuge tubes (15mL, 391 Falcon) to avoid the loss of material due to vial adhesion. $6mL 18\Omega$ milli-Q (MQ) water 392 and 0.131 mL 16 M nitric acid (HNO₃) were added to neutralise the KOH and acidify 393 the solution to 2% for spectroscopic compatibility. Tubes were shaken on a desktop 394 vortex-mixer for five seconds and racked in order of sample age. Blanks of KOH, MQ H₂O and HNO₃ were produced each time a new aliquot of KOH was taken, approxi-396 mately every 5 samples. This procedure and microfossil separation were performed in 397 batches of 10 samples, randomised to avoid any methodological bias after the cleaning 398 stage. 399

Samples were analysed via inductively coupled plasma mass-spectrometry (ICP-MS) (PerkinElmer NexION 350D). 2.5mL of sample solution were nebulised in helium gas and run on an ICP-MS method calibrated for silicon using the SLRS-6 certified reference material. Silicon concentrations were obtained and corrected for contamination by subtracting the mean blank silicon value from the samples. Measures were converted from silicon (Si) concentrations to silica (SiO₂) masses, scaled from 0.45mL aliquots to 0.5mL and divided by the number of particles per sample to produce silica-per-particle.

407 Morphological Measures

408 SEM Imaging

⁴⁰⁹ 14 samples were identified for size measurement that reflected both extreme and ⁴¹⁰ average values of the silica-per-particle time series. A minimum of 12 frustules were ⁴¹¹ individually picked from the 125-150 µm size fraction of each sample using a single-⁴¹² haired paintbrush according to the strict morphological criteria above (Supplementary ⁴¹³ Fig. 6). Frustules were mounted inside-up onto aluminium SEM pin stubs with car-⁴¹⁴ bon adhesive discs. Mounted stubs were checked under a stereo-zoom light microscope

⁴¹⁵ (Leica MZ 95), and additional frustules were picked in case of inversion, surface ⁴¹⁶ crystallization or breakage.

Specimens were mounted onto 12 mm aluminium pin stubs using carbon adhesive and sputter coated with ~15 nm Au/Pd using a Quorum Technologies Q150R ES coating unit. Specimens were then imaged with a scanning electron microscope (Zeiss Sigma 300) under the In-Lens detector to reduce shadows. An electron high tension voltage of 2.00 kV and a working distance of 6.8 mm was used. A range of zoom magnifications from x330 to x400 were tested on sample 49, whilst all other samples were imaged at x400.

424 Digital Processing of SEM Images

Specimen images were exported as .tif raster files and converted to .png. Background 425 removal was done both manually and using Pixelmator Pro [64] and Fiji [65]. Cropped 426 images were loaded into Fiji, the scale set, and the surface area and maximum and 427 minimum Feret's Diameters of the valve and cingulum [28] were measured using inbuilt 428 color thresholding and particle size analysis (Supplementary Fig. 7c,d). Surface poros-429 ity was measured by further cropping to remove the cingulum to isolate the valve, 430 from which the total pore area was isolated using color thresholding and particle size 431 analysis and quantified as a percentage of the valve area (Supplementary Fig. 7e,f). 432 Areolae (pores) [28] were also counted and the mean pore area computed. A macro 433 was written in Fiji to automate this process for the 12-13 frustules per sample. Frus-434 tule thickness was measured using the line tool to measure the cingulum at 0° , 90° , 435 180° and 270°, at which points the width was vertical or horizontal. The width was 436 measured between the two pixels that contrasted the most to their adjacent pixels, a 437 consistent feature across all specimens (Supplementary Fig. 7g-j). The mean of these 438 four thicknesses was computed for each frustule. 439

The mean frustule area, maximum and minimum Feret's diameters, porosity, and frustule thickness were calculated for each sample from its 12-13 constituent frustules. Following color thresholding, individual frustules were assigned a value 0-3 relating to how completely the pores were resolved; frustules scoring 2 or 3 (badly resolved) were omitted from the sample mean porosity.

445 X-Ray Fluorescence Analysis

Downcore variations in a suite of 44 element intensities including silicon and bromine in 446 RAPiD-21-3K were analyzed using the ITRAX X-Ray Fluorescence (XRF) core scan-447 ner at the British Ocean Sediment Core Research Facility (BOSCORF), Southampton, 448 U.K. Sample resolution was every 2 mm (approximately every 1.6 years), beginning 440 at 1.63 mm depth and ending at 999.63 mm depth. However, topcore intensities 450 from 1.63mm to 27.63mm depth (2004–1986 CE) were omitted due to their erratic-451 ity. The intensities were calibrated against the weight percentages of 25 oxides and 452 elements previously collected via Wavelength Dispersive X-Ray Fluorescence Spec-453 troscopy (WDXRF) from a sample core, AU10v. AU10v had also been previously 454 scanned using an ITRAX XRF scanner and calibrated using the following model [44]. 455 The calibration was performed in the ItraXelerate 2.5 model in MATLAB 2014b [66], 456 which uses a multivariate log-ratio calibration with Partial Least Squares regression 457 to map the XRF-derived intensities onto weight percentages by mass [44]. 458

The output weight percentages of silica (SiO₂) and bromine (Br) were multiplied by the linearly interpolated downcore dry-bulk density and sedimentation rate (see Chronology) to give the mass flux of silica or bromine to the sediment (Supplementary Fig. 8a-d). The silica mass flux was further divided by silica-per-diatom to give the number flux of diatoms to the sediment (Supplementary Fig. 8e-g). This latter flux gives the flux of individual valves, as although diatoms are composed of two valves and a girdle band, we did not directly measure the mass of silica in girdle bands.

466 Chronology

The age-model was produced using four carbon-14 accelerator mass-spectrometry val-467 ues from Sicre et al. [63], which were taken approximately every 20cm into the kasten 468 core RAPiD-21-3K, and six lead-210 values from Boessenkool et al. [67], which were 469 taken every 2cm into the box core RAPiD-21-12B (Supplementary Table 1). Prior 470 coarse-fraction analysis of RAPiD-21-3K and RAPiD-21-12B suggested sufficient over-471 lap to employ the box core lead ages to date the recent portion of RAPiD-21-3K. ¹⁴C 472 values were corrected for the Reservoir Effect [68] and calibrated to calendar years 473 using the IntCal09 and CALIB 6.0 programs [69]. ²¹⁰Pb counts were plotted against 474 core depth and six values from the initial linear region of the exponential were con-475 verted to calendar years using the radioactive decay equation $(\lambda = 22.26 \text{yrs})$ [70]. A 476 fifth-order polynomial was fitted to give an age-depth model for the investigated times-477 pan and to account for variable sedimentation rates (Supplementary Fig. 9). The total 478 sedimentation rate was 1 cm/8.02 yrs, facilitating resolution of decadal (10^{1}yr) excur-479 sions. This age-model was applied to all datasets used in this investigation excluding 480 the sortable silt data, which were already dated in Moffa-Sánchez & Hall [71]. 481

482 **Error**

483 Sources of Uncertainty

The 'Instrument Detection Limit', for the mass spectrometry analysis applied to deter-484 mine silica-per-particle, was determined as 5.66ppb Si from three standard deviations 485 of the washes. The minimum measured was 141.36ppb Si, so was confirmed as sig-486 nal rather than instrument noise. In the performed method there were four sources 487 of uncertainty: instrument precision, variation in background silicon contaminating 488 the KOH and HNO₃ solutions, samples randomly not reflecting the true silica-per-489 particle and human error in counting the number of particles dissolved. The relative 490 standard deviation (RSD) of the replicate samples should incorporate all four sources 491

of uncertainty. However, the measured RSD was only highest for silica-per-radiolarian
(RSD=9.23%), so the higher value of the relative standard deviation in the blanks
(see Spectroscopic Analysis) was employed for silica-per-diatom (RSD=7.33%).

⁴⁹⁵ Uncertainty in the frustule size measures was greatest in the removal of the SEM ⁴⁹⁶ image background, as the recognition software may fail to remove additional detritus ⁴⁹⁷ or shadows on the outside of the frustule. These might have locally increased the ⁴⁹⁸ frustule size and affect the maximum Feret's Diameter to a greater extent than the ⁴⁹⁹ frustule area. Uncertainty in frustule thickness measurement lay with the minimum ⁵⁰⁰ resolution of the .png images, as thicknesses can only be correct to the nearest pixel. ⁵⁰¹ The standard error for all morphological measures was calculated for each sample.

502 Outliers

Outliers were identified as values that were more than three scaled median absolute 503 deviations from the median [72]. Outliers matching this criteria were removed from 504 the calibrated X-ray fluorescence datasets prior to the calculation of mass fluxes. No 505 such outliers were present in the silica-per-diatom, frustule area or frustule thickness 506 datasets. Five such outliers were identified in the silica-per-radiolarian dataset. The 507 four outliers greater than the mean were included in Fig. 1 and the associated trend 508 and range analysis as they visually appeared to align with local maxima in the silica-509 per-diatom dataset. Even if these outliers were excluded, the silica-per-radiolarian 510 linear decline would remain statistically significant at the 5% level (p=0.0178). 511

512 Statistical Tests

513 Statistical tests were performed in MATLAB R2024a using the Statistics and Machine

Learning Toolbox and the Signal Processing Toolbox [73, 74].

515 Data Filtering

Simple moving averages were applied to the SPG index barometric streamfunction with an 11-point window length (Fig. 3d), and to the temperature reconstructions in Fig. 4c-f with 50, 50, 4, and 3-point window lengths respectively to reflect 50-year periods.

Savitzky-Golay filtering [75] is a form of moving average that uses a polynomial fit rather than a linear fit to filter data, and so is useful for large noise data. Savitzky-Golay filtering was applied to the reconstructed [36] and observed [37] NAO index, the sortable silt [71], and the AMO index [41] datasets. The polynomial order applied to all datasets was 4 and the frame length was determined using the Nyquist-Shannon theorem [76] independently for all datasets, giving $\pm 73/2$ data-points for the NAO index.

527 Bivariate Pearson's Correlation

The bivariate Pearson's Correlation was used to test the alternative hypothesis that there was a statistically significant linear correlation between calendar age (x) and another variable (y) over the entire 788 yr record against the null hypothesis that there was no such statistically significant linear correlation.

The y variables on which this test was applied were both silica-per-particle datasets, frustule area, and frustule thickness. For these tests, the y values from the excursion E_4 (1934–1971 CE) (see Main) were omitted. This test was two-tailed as it tested for both positive and negative correlations, so the maximum p-value for statistical significance at the 5% level was 0.025.

537 Moving Pearson's Correlation

The moving Pearson's Correlation was used to test the alternative hypothesis that there was a statistically significant, positive, linear correlation between a fluctuating variable (x) and silica-per-diatom (y) over a moving window. Such x variables were the reconstructed [36] and observed [37] NAO index, the sortable silt mean grain size [71], and the reconstructed AMO index [41]. The moving window applied to the NAO index was $\pm 73/2$ years from the sample value, the sortable silt was $\pm 17/2$ years, and the AMO index was $\pm 77/2$ years. These were tested against the null hypothesis that there was no such statistically significant linear correlation over the defined window.

The silica-per-diatom dataset of 55 data points was interpolated using spline interpolation to give 805 silica-per-diatom values at corresponding ages to the NAO data-points for this correlation, 196 at corresponding ages to the sortable silt data-points, and 788 at corresponding ages to the AMO data-points. All the tests were one-tailed, testing for a positive correlation, so the maximum *p*-value for statistical significance at the 5% level was 0.05. The Bonferroni Correction [77] was not applied.

552 Bivariate Spearman's Rank Correlation

The bivariate Spearman's Rank Correlation was used to test the alternative hypothesis that there was a statistically significant monotonic correlation between an independent variable (x) and a dependent variable (y) over the entire 788-yr record against the null hypothesis that there was no such statistically significant monotonic correlation.

This test was used to determine the correlation between each morphological measure (x) and unchanged or detrended silica-per-particle (y), between sortable-silt mean grain size (x) [71] and silica-per-diatom (y), and between the sea-surface temperature reconstructions and the bromine mass flux of Fig. 4 (x) [46-49] and sedimentary diatom flux (y). This test was two-tailed as it tested for both positive and negative

correlations, so the maximum p-value for statistical significance at the 5% level was 0.025.

564 Analysis of Covariance

The Analysis of Covariance (ANCOVA) was used to test the alternative hypothesis 565 that there was a statistically significant difference between the two gradients of the 566 linear trendlines applied to the silica-per-particle data values between 1213–1756 CE 567 and 1774–2001 CE. For this test, the silica-per-radiolarian outliers were omitted, but 568 the values from the excursion E_4 (1934–1971 CE) (see Main) were included, in case 569 this excursion was a result of anthropogenic forcing. As the ANCOVA test is based 570 on the asymmetric F-distribution, the maximum p-value for statistical significance at 571 the 5% level was 0.050. Two groups were investigated in each test, so the degrees of 572 freedom was 1 in both cases. 573

574 Find Abrupt Changes in Signal

The *findchangepts* algorithm in MATLAB 2024a returns the index at which the mean of x changes most significantly. This algorithm was used on the Past1000-R3 simulation of subpolar gyre strength of Moreno-Chamarro et al. [35] in the core-site grid square (x) and on the silica-per-diatom dataset (x). Minimum signal thresholds of 142.9 and 200 were used respectively.

580 Supplementary information.

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Declarations

Some journals require declarations to be submitted in a standardised format. Please check the Instructions for Authors of the journal to which you are submitting to see if you need to complete this section. If yes, your manuscript must contain the following sections under the heading 'Declarations':

- 594 Funding
- Conflict of interest/Competing interests (check journal-specific guidelines for which
- ⁵⁹⁶ heading to use)
- ⁵⁹⁷ Ethics approval Not applicable
- Consent to participate Not applicable
- ⁵⁹⁹ Consent for publication Not applicable
- Availability of data and materials
- 601 Code availability Not applicable
- 602 Authors' contributions
- ⁶⁰³ If any of the sections are not relevant to your manuscript, please include the heading
- ⁶⁰⁴ and write 'Not applicable' for that section.

605 Extended Data

606 References

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