



North Atlantic marine biogenic silica accumulation through the early-to-mid Paleogene: implications for ocean circulation and silicate weathering feedback

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15 **Abstract.** The Paleogene history of biogenic opal accumulation in the North Atlantic provides insight into both the evolution of deep-water circulation in the Atlantic basin, and weathering responses to major climate shifts. However, existing records are compromised by low temporal resolution and/or stratigraphic discontinuities. In order to address this problem, we present a multi-site, high-resolution record of biogenic silica (bioSiO_2) accumulation from Blake Nose (ODP Leg 171B, western North Atlantic) spanning the early Paleocene through late Eocene time interval (~65–34 Ma).
20 This record represents the longest single-locality history of marine bioSiO_2 burial compiled to date and offers a unique perspective into changes in bioSiO_2 fluxes through the early-to-mid Paleogene extreme greenhouse interval and subsequent period of long-term cooling. Blake Nose bioSiO_2 fluxes display prominent fluctuations that we attribute to variations in sub-thermocline nutrient supply via cyclonic eddies associated with the Gulf Stream. Whereas few constraints are available on the bioSiO_2 flux pulses peaking in the early Paleocene and early Eocene, a middle Eocene interval of elevated bioSiO_2 flux between ~46 and 42 Ma is proposed to reflect nutrient enrichment due to invigorated overturning circulation following an early onset of Northern Component Water export from the Norwegian-Greenland Sea at ~49 Ma. Comparison of our North Atlantic record against published Pacific bioSiO_2 flux records indicates a diminished nutrient supply to the Atlantic between ~42 and 38 Ma, interpreted as a response to weakening of the overturning circulation. Subsequently, a deep-water circulation regime favoring limited bioSiO_2 burial in Atlantic and enhanced bioSiO_2 burial in the Pacific was established after ~38 Ma, likely in association with a further invigoration of deep-water export from the North Atlantic. We also observe that Blake Nose bioSiO_2 fluxes through the middle Eocene cooling interval (~48 to 34 Ma) are consistently higher than background fluxes throughout the late Paleocene–early Eocene interval of intense greenhouse warmth. This observation is consistent with a temporally variable rather than constant silicate weathering feedback strength model for the Paleogene, which would instead predict that marine bioSiO_2 burial should peak during periods of extreme warming.
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1 Introduction

Biogenic silica (bioSiO_2) secretion by marine plankton and the subsequent accumulation of biosiliceous marine sediments represent the main output flux in the global silicon cycle (Tréguer and De La Rocha, 2013). The present-day silicon cycle is also closely linked to the carbon cycle, because diatoms — the most successful and efficient bioSiO_2 -secreting plankton group in the modern oceans — are also the key marine primary producers (Smetacek, 1999), responsible for up to 40% of total global net photosynthesis per year. Owing to the ballast effect of their siliceous
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valves, diatoms are extremely efficient at exporting organic carbon (C_{org}) from the surface to the deep ocean and facilitating C_{org} burial in marine sediments (Yool and Tyrrell, 2003). This relationship between the silicon and carbon cycles has profound implications for understanding climate change on both long and short timescales in the past, 45 founded on the premise that sedimentary bioSiO_2 mass accumulation rates (fluxes) represent the rate of bioSiO_2 burial, and, importantly, that the burial rate reflects bioSiO_2 production in surface waters at the time of deposition (Ragueneau et al., 2000; Yool and Tyrrell, 2005).

One fundamental control on marine siliceous plankton production is the amount of dissolved silicon supplied to the oceans from terrestrial silicate weathering, a chemical process that ultimately consumes atmospheric CO_2 and 50 releases silicic acid and alkalinity to the oceans (i.e., when combined with carbonate burial in the oceans; Walker et al., 1981; Fontorbe et al., 2020; Penman et al., 2020). By moderating atmospheric CO_2 , the silicate weathering feedback is postulated to operate as a thermostat, maintaining the Earth's surface within a habitable range of temperatures since early in geological history (Kasting, 2019). In today's rapidly warming world, an accurate understanding of the operation of silicate weathering as a climate feedback mechanism is essential.

55 Past transient greenhouse warming events, such as the 'hyperthermal' events of the early-to-mid Paleogene (Paleocene and Eocene epochs; ~66–34 Ma), offer ancient points of comparison for the present-day warming and future climate scenarios. Existing studies suggest that Paleogene bioSiO_2 accumulation patterns are directly linked to variations in continental weathering on both long (Muttoni and Kent, 2007; Cermeño et al., 2015; Renaudie, 2016) and short (Witkowski et al., 2014; Penman, 2016; Penman et al., 2019) timescales. Additionally, large volumes of diatomite and 60 diatom-rich clays deposited on continental shelves during the early Paleogene (e.g., Oreshkina and Aleksandrova, 2007) suggest that the supply of dissolved silicon from continental weathering under the greenhouse climates exerted a strong influence on marine bioSiO_2 accumulation.

In the modern oceans, deep-water circulation also exerts a major control on marine bioSiO_2 accumulation patterns throughout the ocean basins. Firstly, ocean circulation determines the distribution and concentration of limiting 65 nutrients (N, P, Fe) in deep waters and their upwelling into surface waters where they fuel primary production, and, secondly, circulation impacts bioSiO_2 preservation in seafloor sediments (Ragueneau et al., 2000). Most of the present-day biosiliceous production is focused along continental margins, in areas where diatoms can take advantage of nutrients supplied from continental runoff and coastal upwelling (Malviya et al., 2016). A large proportion of bioSiO_2 , however, is recycled even before settling out of the photic zone (Van Cappellen et al., 2002), since the modern oceans 70 are undersaturated with respect to SiO_2 at all depths. Only a fraction of bioSiO_2 produced in the photic zone therefore reaches the ocean floor, and, furthermore, only a fraction of the exported bioSiO_2 is incorporated into sediments and preserved (Frings, 2017).

Both the strength of the silicate weathering feedback and ocean circulation patterns are believed to have undergone profound changes through the early-to-mid Paleogene as the Earth transitioned from a hothouse, ice-free 75 climate state (e.g., Zachos et al., 2008; Kirtland-Turner et al., 2014; Anagnostou et al., 2016) to an icehouse climate marked by continental-scale ice sheets (Zachos et al., 2001; Miller et al., 2020). Isotopic weathering proxies ($^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^7\text{Li}$) display a broad minimum spanning the late Paleocene through early Eocene interval (Misra and Froelich, 2012), which have been interpreted to indicate either flat continental relief through this period (Froelich and Misra, 2015) or evidence for a variable strength of the negative feedback between climate and silicate weathering (Caves et al., 80 2016). Sea level fall associated with the onset of the Antarctic glaciation at the Eocene-Oligocene Transition (EOT)



(Zachos et al., 1996), and the intensification of the Himalayan orogeny are also thought to have altered the dominant weathering regime by facilitating physical rather than chemical weathering, and by exposing large volumes of fresh rock to erosion and weathering (Cermeño et al., 2015).

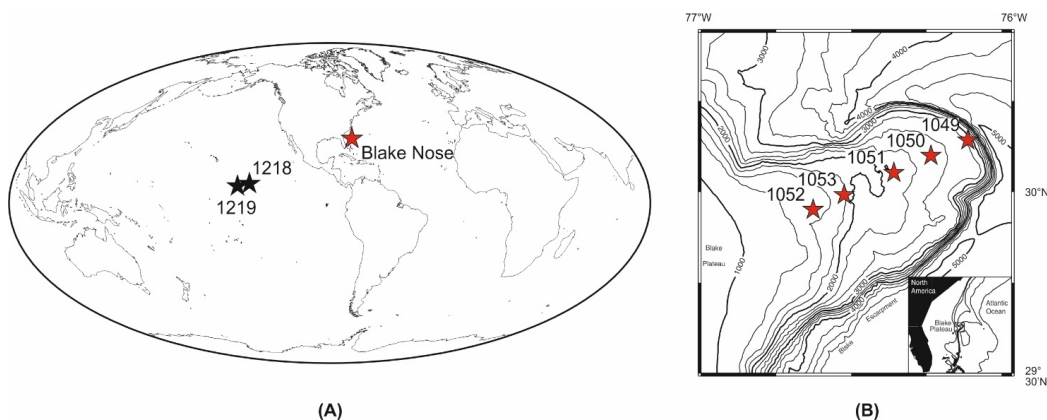
85 The early Cenozoic was a time of low thermal gradients between surface and deep waters and between high and low latitudes, which limited vigorous overturning circulation (Vahlenkamp et al., 2018). There is, however, little consensus on the timing of the onset of Northern Component Water (NCW) production, a precursor to today's North Atlantic Deep Water. Estimates vary from the late early Eocene (~49–50 Ma; Hohbein et al., 2012) through the late Eocene (~38 Ma; e.g., Borrelli et al., 2014; Coxall et al., 2018) to across the EOT interval (~34 Ma; Via and Thomas, 2006; Abelson and Erez, 2017). Regardless, the long-term global cooling spanning the middle and late Eocene (~48–34
90 Ma) is thought to have resulted in enhanced upwelling, and the opening of the Drake Passage is viewed as a milestone in establishing the global pattern of thermohaline circulation in its present-day form in the Atlantic (Via and Thomas, 2006; Abelson and Erez, 2017).

Despite the importance of siliceous biota in the present-day carbon cycle, our understanding of the temporal trends in marine bioSiO_2 accumulation through the early Paleogene is limited. First-order observations indicate an
95 association between peak chert/porcellanite occurrence and deep-water temperatures through the Early Eocene Climatic Optimum (EECO) (Muttoni and Kent, 2007) and during short-lived hyperthermal events of the early Eocene (Penman et al., 2019). The rapid cooling at the end of the Eocene is also widely regarded as the period of diatom proliferation and diversification, especially in the Southern Ocean (Egan et al., 2013; Lazarus et al., 2014; Renaudie, 2016). However, trends in marine bioSiO_2 accumulation in the period between these temporally broadly isolated events representing
100 contrasting climate states, are not well understood. The longest currently available perspective on marine bioSiO_2 accumulation (Cretaceous through Miocene) is based on Deep-Sea Drilling Project (DSDP) Leg 1 through 44 smear-slide data (i.e., data gathered between 1968 and 1978) converted to mass accumulation rates and binned into 10-million-year (Myr) increments (Miskell et al., 1985). Direct sediment measurements of bioSiO_2 concentrations (with calculated fluxes) through the Paleogene are sparse (e.g., Diester-Haass, 1995; Salamy and Zachos, 1999; Diekmann et al., 2004;
105 Lyle et al., 2005; Iwasaki et al., 2014), and mostly focus on restricted time windows of the late Eocene through early Oligocene interval. A major reason for this is that bioSiO_2 is highly vulnerable to water-column and seafloor dissolution, which results in early Paleogene siliceous phytoplankton occurrences often being confined to narrow stratigraphic intervals at many sites (see Barron et al., 2015; Witkowski et al., 2020b).

The observations summarized above provoke three fundamental questions: (1) How did bioSiO_2 burial flux
110 evolve through the early-to-mid Paleogene?; (2) What were the main controls on changes in marine bioSiO_2 burial in this time interval?; and (3) What was the bioSiO_2 burial response to long-term Paleogene climate changes? Through the early Paleogene, bioSiO_2 accumulation was largely focused in the Atlantic and on the Eurasian Platform (Miskell et al., 1985; Muttoni and Kent, 2007; Moore et al., 2008; Barron et al., 2015; Wade et al., 2020). Unusually expanded lower Paleocene through upper Eocene biosiliceous successions were recovered from Blake Nose in the mid-latitude western
115 North Atlantic (Shipboard Scientific Party, 1998a-f; Witkowski et al., 2020a). In order to gain a quantitative insight into how bioSiO_2 burial evolved through the early Paleogene hothouse and the ensuing period of global cooling, we have generated a composite high-resolution Blake Nose bioSiO_2 flux record from ~65 to 34 Ma, spanning nearly the entire Paleocene and Eocene epochs. This work follows on from two previous publications with a focus on the Blake Nose early-to-mid Paleogene siliceous microfossils: (1) Witkowski et al. (2020a), in which a revised chronological



120 framework is proposed for Site 1050 and 1051, and (2) Witkowski et al. (2020b), in which Paleogene trends in chert and porcellanite occurrences were compared to spatial and temporal patterns in Atlantic biosiliceous sediment occurrences. Here, we aim to determine the main controls on bioSiO_2 fluxes in a key locus of biosiliceous accumulation in the Northwest Atlantic (Blake Nose) during the early-to-mid Paleogene – a period of Cenozoic climate change characterized by profound variations in global temperature.



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Figure 1. Maps showing the location of sites considered in the present paper. (A) Blake Nose (red star) in the western North Atlantic and Eastern Equatorial Pacific sites (black stars). Base map generated using Ocean Drilling Stratigraphic Network Advanced Plate Tectonic Reconstruction service (www.odsnet.de). (B) Location of the Ocean Drilling Program (ODP) Leg 171B sites on Blake Nose. Modified from Shipboard Scientific Party (1998a).

ODP Hole	Latitude	Longitude	Water depth (m)	Reference	Number of samples examined for bioSiO_2
1049A	30°08.5436'N	76°06.7312'W	2656.1	Shipboard Scientific Party (1998b)	70
1050A	30°05.9977'N	76°14.1011'W	2299.8	Shipboard Scientific Party (1998c)	273
1050C	30°05.9953'N	76°14.0997'W	2296.5	Shipboard Scientific Party (1998c)	7
1051A	30°03.1740'N	76°21.4580'W	1982.7	Shipboard Scientific Party (1998d)	762
1052B	29°57.0791'N	76°37.6098'W	1345.0	Shipboard Scientific Party (1998e)	13
1052F	29°57.0794'N	76°37.6094'W	1343.5	Shipboard Scientific Party (1998e)	26
1053A	29°59.5385'N	76°31.4135'W	1629.5	Shipboard Scientific Party (1998f)	79



				Total samples examined	1230
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130 **Table 1.** Sites included in this study, along with geographic coordinates, site chapters, and number of samples examined for bioSiO_2 . Sites used for bioSiO_2 flux calculations are underlined.

2 Materials and methods

2.1 Study sites and stratigraphy

135 This study is focused on drillcores recovered as part of the Ocean Drilling Program (ODP) Blake Nose Paleooceanographic Transect and includes Holes 1049A, 1050A/C, 1051A, 1052B/F and 1053A (Shipboard Scientific Party, 1998b-f) (Fig. 1) (Table 1). The transect was drilled on Blake Nose (BN; also often referred to as ‘Blake Ridge’) in the western North Atlantic Ocean in order to reconstruct the Cretaceous-Paleogene paleooceanographic history of the region adjacent to the South Atlantic Bight (Shipboard Scientific Party, 1998a), offshore of the southeastern U.S. seaboard between Florida Straits and Cape Hatteras (Gula et al., 2016). The BN is a northeast-trending extension of the
140 Blake Plateau comprised of a Cretaceous to Paleogene continental margin succession (Pinet et al., 1981; Shipboard Scientific Party, 1998a) (Fig. 1B). As Paleogene sediments draping BN were deposited on the seaward slope of a large reef formed in the Early Cretaceous, the transect sites likely retain the relative depths of the paleo reef system (Shipboard Scientific Party, 1998a). Drilling at BN, as well as at sites further north along the North American margin, documented well-preserved early Paleogene siliceous microfossils (e.g., Gombos, 1982; Nishimura, 1992; Hollis,
145 2014). The BN transect sites that recovered the most expanded early-to-mid Paleogene sections (Sites 1050 and 1051) include only a few narrow chert and porcellanite-bearing intervals (Witkowski et al., 2020b), and sparse clinoptilolite occurrences, which suggests minimal diagenesis of sedimentary bioSiO_2 . As such, the good overall preservation of siliceous microplankton in Paleogene sediments at BN, combined with the exceptionally long stratigraphic span of the record recovered during Leg 171B (Witkowski et al., 2020a, and references therein), makes the BN transect especially
150 well-suited for reconstructing variations in bioSiO_2 burial flux in the early Paleocene through late Eocene time period. To this end, we examined 1230 samples from five BN drillsites: Sites 1049, 1050, 1051, 1052, and 1053.

Site 1049 is the most distal and deepest site included in this study (1000–2000 m paleodepth; Shipboard Scientific Party, 1998b) (Fig. 1B; Table 1). The Paleogene section of Hole 1049A was poorly recovered due to the extensive presence of chert horizons. As a consequence, numerous biostratigraphic datums are poorly constrained
155 through the recovered sequence, and age control is only approximate, especially through the Early-Middle Eocene Transition (EMET). Based on the recent revisions to the bio-magnetostratigraphy of Holes 1050A and 1051A, however, Witkowski et al. (2020b) proposed a revised age model for the Paleocene through Eocene interval of Hole 1049A. Here, we examine 70 samples from the chert-free, siliceous microfossil-bearing interval of Hole 1049A, spanning Cores 1049A-3H through -12X (~21.1 to 88.1 compacted meters below seafloor [cmbsf – see Witkowski et al., 2020a]; Table
160 1). Due to incomplete recovery and the temporal patchiness of the record, however, we do not include data from Hole 1049A in bioSiO_2 flux calculations.

Site 1050 (1000–2000 m paleodepth; Shipboard Scientific Party, 1998c) was drilled several km upslope of Site 1049 (Fig. 1B; Table 1). The Paleogene succession cored in Holes 1050A and 1050C is considerably more expanded and stratigraphically more complete than in Hole 1049A. Siliceous microfossils occur throughout the succession cored
165 in Hole 1050A, but in Hole 1050C siliceous microfossils are confined to Core 1050C-2R (Witkowski et al., 2020b). We



apply the age model of Witkowski et al. (2020a), who interpreted the presence of two major stratigraphic gaps. For this study, we examined 273 samples from Hole 1050A (Cores 1050A-2H through -36X; ~11 to 319.3 cmbsf) and 7 samples from Hole 1050C (Core 1050C-2R; 328 to 336 cmbsf).

170 Site 1051, the intermediate-depth site of the BN Transect (1000–2000 m paleodepth; Shipboard Scientific Party, 1998d) (Fig. 1B; Table 1), recovered the most expanded lower Paleocene through upper Eocene succession among Leg 171B sites. Siliceous microfossils occur throughout this succession, except for within several narrow dissolution intervals (for details see Witkowski et al., 2020b). We use the age model of Witkowski et al. (2020a), who showed that the Hole 1051A succession is interrupted by two major gaps that are broadly correlative to the hiatuses in Hole 1050A (see also Röhl et al., 2003). A total of 762 samples from the entire succession cored at Hole 1051A (~8.5 to 175 644 cmbsf) were examined for this study.

Site 1052 is the shallowest site of the BN transect sites, drilled near the crest of the BN (Fig. 1B; Table 1). Most of the middle bathyal (600–1000 m paleodepth; Shipboard Scientific Party, 1998e) Paleogene succession at this site is truncated by a prominent hiatus. In this study, we include a narrow composite interval of Holes 1052B and 1052F (~77 to 131 meters composite depth [mcd]) spanning the Middle-Late Eocene Turnover (MLET) (Kamikuri and Wade, 180 2012). As this interval overlaps with parts of Holes 1051A and 1053A, it is not considered in sediment flux calculations. For age control at Site 1052, we use the bio-magnetostratigraphic constraints from Shipboard Scientific Party (1998e), Ogg and Bardot (2001), and Wade et al. (2012), following Witkowski et al. (2020b). A total of 39 samples from Site 1052 were used in this study.

185 Site 1053 was drilled between Sites 1051 (intermediate depth) and 1052 (shallowest depth), in the upper part of the BN transect (500–700 m paleodepth; Shipboard Scientific Party, 1998f) (Fig. 1B; Table 1). Site 1053 recovered an expanded siliceous microfossil-rich upper Eocene section with no detectable stratigraphic gaps, as indicated by the age model of Borrelli et al. (2014). At total of 79 samples from Hole 1053A (~0.5 to 183 meters below sea floor [msbf]) were examined for this study.

190 Despite two major discontinuities and multiple recovery gaps, our composite BN record is comprised of data from five sites, and spans the earliest Paleocene (~64.74 Ma; Magnetochron C28n in Hole 1051A, Witkowski et al., 2020a) through latest Eocene (~33.94 Ma; Magnetochron C13r in Hole 1053A; Borrelli et al., 2014) interval. This composite represents the longest currently available single-locality record of deep-sea biosiliceous sedimentation through the Paleogene. We report all ages relative to the Gradstein et al. (2012) timescale, hereafter referred to as GTS2012.

195 2.2 $^{29}\text{SiO}_2$ measurements

200 $^{29}\text{SiO}_2$ concentrations were determined by means of a Hach DR-3900 spectrophotometer, using Hach method 8186 (heteropoly blue method). All spectrophotometric analyses closely followed the wet alkaline extraction procedure of Olivarez Lyle and Lyle (2002). Unlike Olivarez Lyle and Lyle (2002), however, for base extraction we used 1M KOH and 10 mg ground sediment subsamples rather than 2M KOH and 20 mg subsamples. This was done in order to avoid SiO_2 polymerization (Annette Olivarez Lyle, written communication, 2015), manifested by the precipitation of whitish filaments in test tubes following base extraction conducted at higher KOH concentrations with larger



subsamples. bioSiO_2 concentrations for individual sites are tabulated in Supplementary Tables S1 through S5, and data used for bioSiO_2 flux calculations are presented in Supplementary Figures S1–S3 in the online Supplementary Materials.

205 Three methods were employed to monitor analytical precision of the bioSiO_2 measurements: (1) One sample in each analyzed batch was subject to stepwise standard addition against a target curve, using liquid SiO_2 standard supplied by Hach (average target curve $R^2=0.994$, $n=84$); (2) One random sample from every sample batch was also analyzed in duplicate, with good correlation between duplicate analyses (average $R^2=0.98$, $n=92$; online Supplementary Materials Fig. S4); and (3) one of three in-house consistency standards was analyzed in approximately every second sample batch.

210 2.3 Sediment mass accumulation rate calculations

All sediment mass accumulation rate (hereafter: flux) values in this work are expressed as $\text{g/cm}^2/\text{thousand years}$ (kyrs), and are calculated using standard terms from previous studies (e.g., Diester-Haass, 1995; Piela et al., 2012; D'haenens et al., 2014):

$$215 \quad \text{MAR} (\text{g/cm}^2/\text{kyrs}) = \text{sedimentary component} [\text{g component/g bulk sediment}] \times \text{linear sedimentation rate (LSR)} [\text{cm/kyr}] \times \text{sediment dry bulk density (DBD)} [\text{g/cm}^3]$$

220 Use of magneto-biostratigraphic age models to establish LSRs typically produces unrealistic jumps in sediment flux estimates at magnetostratigraphic boundaries, with order-of-magnitude differences between consecutive age-model tiepoints. In order to smooth out such abrupt features, which we deem to be artifacts of the applied age models, in our flux records, we fitted polynomial regressions against the age vs depth curves (or segments thereof comprised between hiatuses), following the approach of Piela et al. (2012). The datasets developed in the present work are based on several holes that include several hiatuses, and robust age models that are consistent between holes are essential to obtain a reliable composite stratigraphy. We therefore plot the flux records derived from smoothed LSR estimates using ages interpolated from the original (i.e., non-smoothed) age-depth curves (Figs S1–S3).

225 Sediment flux studies often estimate wet bulk sediment density through calibration of high-resolution estimates of wet bulk density (obtained via gamma ray attenuation [GRA] analysis) against discrete DBD measurements collected during routine shipboard analysis. In the present work, establishing a single GRA–DBD correlation over the entire cored interval proved ineffective for Sites 1050 and 1051, likely due to the downhole increase in compaction. Instead, we estimated DBD for a given depth by interpolating between shipboard discrete DBD measurements (Shipboard Scientific Party, 1998b–d, f). Sediment density plots, LSRs, and calculated fluxes are included in the online
230 Supplementary Materials (Figs S1–S3 and Tables S2–S3, S5).

2.4 Stable isotope and $p\text{CO}_2$ data

235 Our interpretation of possible controls on early-to-mid Paleogene bioSiO_2 accumulation is based on comparison to published isotopic weathering ($^{87}\text{Sr}/^{86}\text{Sr}$, $^{187}\text{Os}/^{188}\text{Os}$ and $\delta^7\text{Li}$; Ravizza et al., 2001; Ravizza and Peucker-Ehrenbrink, 2003; Misra and Froelich, 2012; Klemm et al., 2005) and paleocirculation proxies ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$; Cramer et al., 2009), as well as the recent atmospheric $p\text{CO}_2$ reconstruction (Foster et al., 2017), and silicate weathering flux model (hereafter SWF) (Caves et al., 2016). For further discussion and a full documentation of data sources see the online Supplementary Materials (Supplementary Text and Figure S5).



2.5 Statistical treatment

Smoothed long-term trends in bioSiO_2 flux and published geochemical records were obtained via LOESS
240 regression (Cleveland et al., 1992), computed using R Studio v. 3.5.1. Statistical analysis was performed on smoothed
time series (bioSiO_2 flux, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $p\text{CO}_2$, $^{87}\text{Sr}/^{86}\text{Sr}$, $^{187}\text{Os}/^{188}\text{Os}$, $\delta^7\text{Li}$ and SWF) using Statistica 13.1 package.

The degree of covariance of the analyzed variables was assessed by correlation analysis. Normality test
procedure was carried out for all variables using the Shapiro-Wilk test ($\alpha=0.05$). The Pearson correlation coefficient was
used to assess covariance for each pair of variables characterized by a normal distribution. The non-parametric Spearman
245 correlation coefficient was used when non-normal distribution was indicated for a given variable by the Shapiro-Wilk
test.

The analysis also involved a multiple regression model, which describes the relationship of the dependent
variable Y with a set of independent variables X_1, X_2, \dots, X_k (which, in this study, is the relationship between bioSiO_2 flux
and other proxy records). It is defined by Eq. (1):

$$250 \quad Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \dots + \beta_k X_k + \xi \quad (1)$$

Where:

β_j – model parameters (regression coefficient)

ξ - random component

255 The parameters of the regression equation are estimated using least squares method, and determination coefficient and
standard error of estimation are used to assess the goodness of the model.

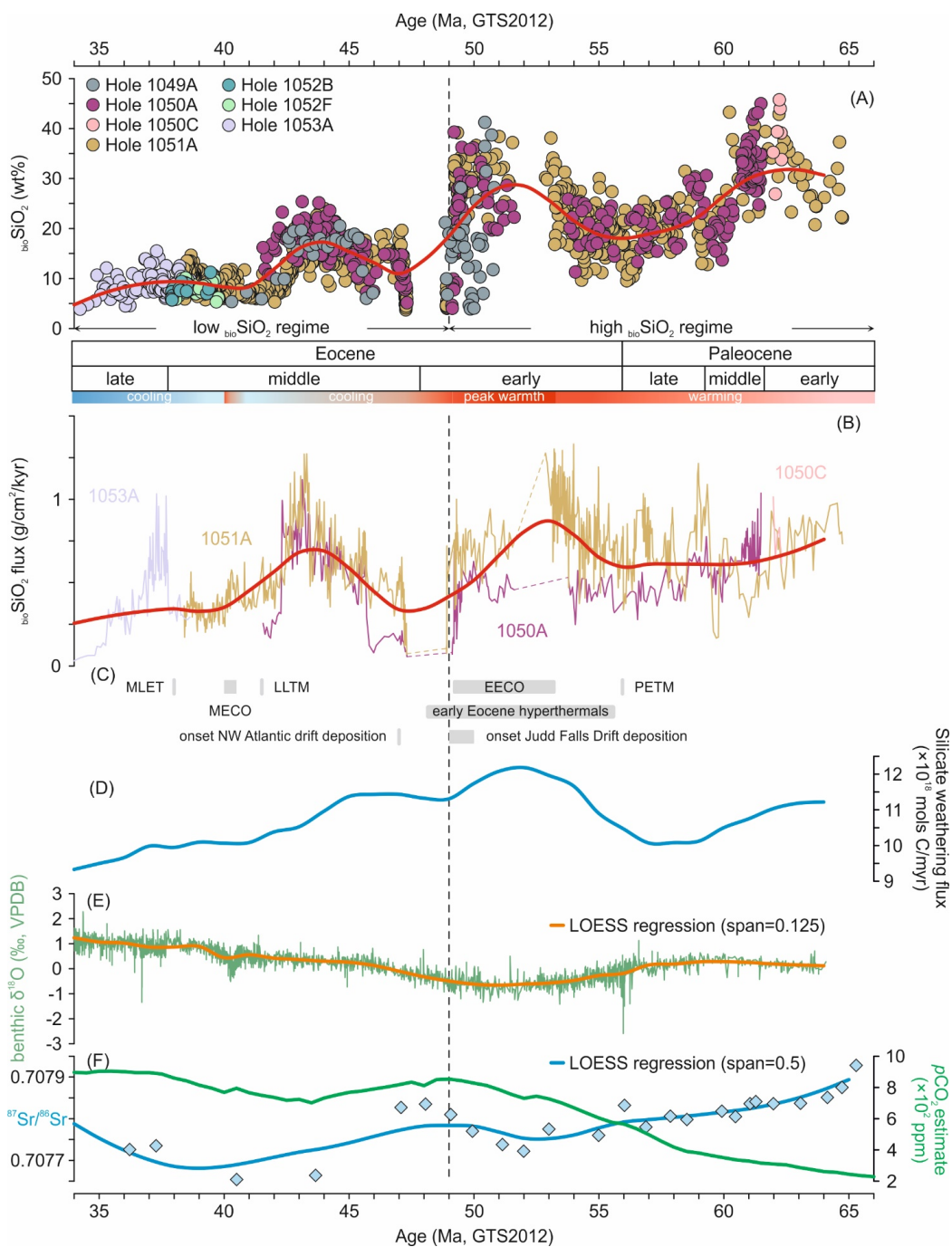


Figure 2. Composite Blake Nose weight per cent biogenic silica concentrations (A) and fluxes (B) through the early-to-mid Paleogene plotted against key tectonic and climatic events (C), silicate weathering flux as modelled by Caves et al. (2016) (D), global benthic foraminiferal $\delta^{18}\text{O}$ compilation of Cramer et al. (2009; rescaled to GTS2012) (E), and $p\text{CO}_2$ reconstruction (Foster et al., 2017) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Misra and Froelich, 2012) (F). Schematic representation of



climatic trends next to chronostratigraphy panel is consistent with Cramwinckel et al. (2018). Abbreviations: wt% - weight per cent; bioSiO_2 - biogenic silica; GTS2012 - Geologic Time Scale 2012, see Gradstein et al. (2012).

3 Results and interpretation

265 Our new composite bioSiO_2 record from Blake Nose spans the interval between ~65 and 34 Ma (Fig. 2A), representing the longest single-locality record of bioSiO_2 concentrations compiled to date. The composite record, however, lacks data in two short time windows: between ~53.5 and 52.0 Ma (Magnetochrons C24n through C23n) and between ~47.5 and 49.0 Ma (i.e., through the EMET). This is due to the presence of prominent hiatuses at all study sites spanning these intervals (Shipboard Scientific Party, 1998b-d; Witkowski et al., 2020a) (Fig. 2A).

270 The BN bioSiO_2 composite shows variable but generally high values between ~65 and 49 Ma (Fig. 2A). Two broad bioSiO_2 maxima are observed within this high- bioSiO_2 interval, culminating at ~61.5 Ma and at ~51.5 Ma (Fig. 2A). These maxima are separated by a broad low in bioSiO_2 with a nadir centered at approximately the Paleocene-Eocene boundary (~56 Ma). From ~49 Ma to the end of the record at ~34 Ma, bioSiO_2 levels are considerably lower and less variable (Fig. 2A), with a distinct maximum culminating at ~44 Ma.

275 Long-term trends in BN bioSiO_2 fluxes are calculated based on a composite record built from datasets generated from Sites 1050, 1051, and 1053. Through the Paleocene and early Eocene, Site 1050 generally displays lower bioSiO_2 fluxes than Site 1051 (Fig. 2B). From ~46 to 34 Ma, both bioSiO_2 flux trends and values are remarkably consistent between Sites 1050 and 1051 (Fig. 2B). The short time interval in which records from Site 1051 and Site 1053 overlap also reveals coherent bioSiO_2 flux values (Fig. 2B). Thus, following a period of high inter-site variability through the
280 Paleocene, three intervals of elevated bioSiO_2 fluxes are observed, which are consistent between sites and peak at ~53.2 Ma, ~43.3 Ma, and at ~37.7 Ma. The overall patterns in bioSiO_2 and bioSiO_2 flux estimates are also consistent, especially through the middle and late Eocene. Most importantly, however, the bioSiO_2 flux values fall within the same order of magnitude through most of the study period (except for peak bioSiO_2 fluxes at Site 1051 between 54 and 53 Ma and from 44 to 43 Ma). Furthermore, our record consistently shows that bioSiO_2 fluxes through the middle Eocene
285 cooling were, on average, higher than (Site 1050) or similar to (Site 1051) bioSiO_2 fluxes through the early Eocene period of extreme greenhouse warmth (Fig. 2B).

3.1 Impact of hiatuses and diagenesis on BN bioSiO_2 flux estimates

The records from Sites 1050 and 1051, which constitute the older part of the composite presented here, are interrupted by hiatuses. These discontinuities in the BN record could introduce a bias to the flux estimates, for instance
290 by influencing the LSR calculations. The age models for Holes 1050A/C and 1051A used in this study (see Witkowski et al., 2020a, for details), however, are highly consistent in that the hiatuses are identified in correlative intervals, and – furthermore – LSRs used in flux calculations were subjected to polynomial smoothing, which should eliminate most short-term artifacts imposed by age model imperfections. bioSiO_2 flux estimates could also be compromised by winnowing, which could concentrate biosiliceous particles over some areas of the seabed, while removing them from
295 adjacent areas. In the core description logs for BN sites included in the present bioSiO_2 flux reconstruction, explicit mention of winnowing is made only in one instance, i.e., for Core 1051A-41X (Shipboard Scientific Party, 1998d). This core also includes abundant zeolite crystals (J. Witkowski, unpub. observations), which are an indicator of bioSiO_2 diagenesis (see Fenner, 1991). For this reason, Core 1051A-41X was excluded from the present study. Also, no



300 %_{bio}SiO₂ measurements were performed on the sparse cherty or porcellanitic intervals at Sites 1050 and 1051. Scanning
electron micrograph examination of diatoms from the remaining intervals of the BN composite indicates only minor
diagenetic effects on the siliceous microfossils, manifested mostly by the dissolution of the most delicate parts of the
valves, such as areole occlusions or pore fields. For these reasons, the _{bio}SiO₂ fluxes reconstructed in this study are
deemed to be robust.

3.2 Controls on _{bio}SiO₂ accumulation through the early-to-mid Paleogene at Blake Nose

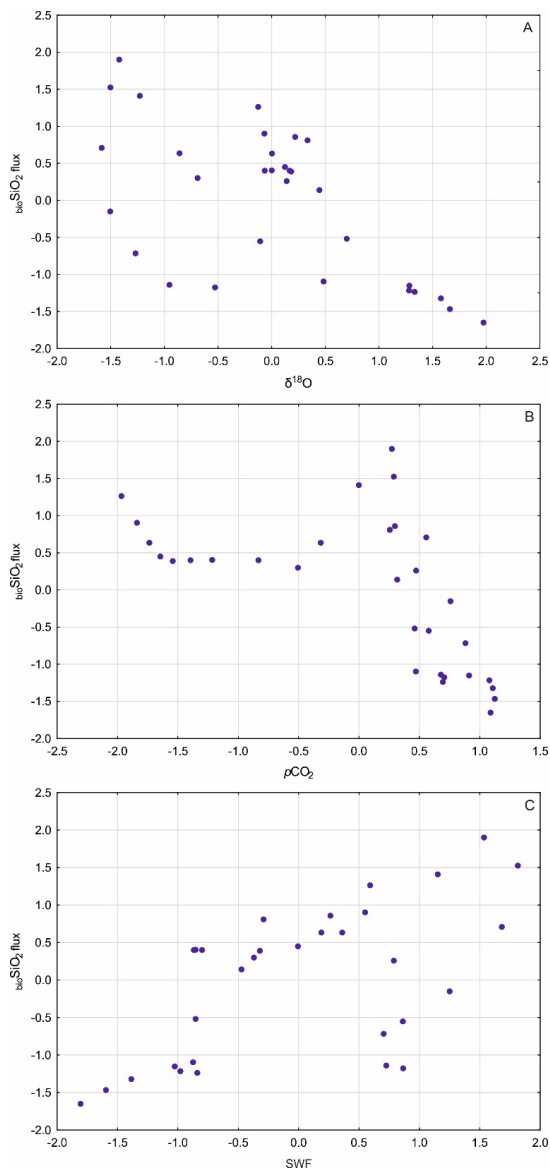
305 _{bio}SiO₂ production, export, and preservation in marine sediments are influenced globally by dissolved silicon
supply to the oceans derived from terrestrial weathering, which is closely linked to climate via a negative feedback
(e.g., Walker et al., 1981), and by ocean circulation patterns and upwelling, which supply the bulk of nutrients to
surface waters (Miskell et al., 1985; Handoh et al., 2003). In order to gain insight into the influence that each of these
factors has exerted on _{bio}SiO₂ accumulation through the early-to-mid Paleogene at Blake Nose, we compared the _{bio}SiO₂
310 flux composite record to published composite global benthic foraminiferal δ¹⁸O and δ¹³C records, *p*CO₂ proxy
estimates, proxy records of continental weathering (⁸⁷Sr/⁸⁶Sr, ¹⁸⁷Os/¹⁸⁸Os and δ⁷Li), and modelled silicate weathering
flux (SWF) (Fig. 2, Fig. S5).

We find that _{bio}SiO₂ flux is moderately correlated to modelled SWF (*r*=0.597, *p*<0.05), and more strongly, but
inversely correlated to both *p*CO₂ (*r*=-0.775, *p*<0.05), and δ¹⁸O (*r*=-0.618, *p*<0.05) (Fig. 3). A weaker, but still
315 statistically significant, correlation exists between _{bio}SiO₂ flux and δ⁷Li (*r*=-0.473, *p*<0.05), ¹⁸⁷Os/¹⁸⁸Os (*r*=0.430,
p<0.05), and ⁸⁷Sr/⁸⁶Sr (0.418, *p*<0.05) (Fig. 3). No statistically significant correlation has been found between _{bio}SiO₂
flux and trends in benthic foraminiferal δ¹³C. These relationships suggest that overall, through the early-to-mid
Paleogene, _{bio}SiO₂ flux at BN was indirectly shaped by a combination of changes in atmospheric greenhouse gas levels,
bottom water temperatures (assuming ice-free poles through our study period), and supply of solutes from terrestrial
320 silicate weathering.

Multiple regression indicates four significant variables shaping BN _{bio}SiO₂ flux: δ¹⁸O, *p*CO₂, δ¹³C, and
⁸⁷Sr/⁸⁶Sr. Except for δ¹³C, this is consistent with the correlations discussed above. Notably, SWF was excluded by the
multiple regression model. This is likely due to the high overall similarity in temporal trends displayed by BN _{bio}SiO₂
flux and SWF. The multiple regression model equation takes the form:

325
$$\text{bioSiO}_2 \text{ flux} = 798.57 - 0.156 \times \delta^{18}\text{O} - 0.0008 \times p\text{CO}_2 - 0.111 \times \delta^{13}\text{C} - 1126.58 \times {}^{87}\text{Sr}/{}^{86}\text{Sr}$$

This model explains ~71% of BN _{bio}SiO₂ flux variance, with a standard error of estimation equal to 0.09. We find that
the model reproduces our calculated _{bio}SiO₂ flux values reasonably well (Fig. 2B). Thus, both the correlations and
multiple regression suggest that BN _{bio}SiO₂ flux was shaped mostly by δ¹⁸O, *p*CO₂, and the supply of continental
weathering products – all of which are related to the temperature–silicate weathering feedback.



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Figure 3. Correlation scatter plots for the three strongest statistical relationships identified in the present study: biogenic silica flux versus $\delta^{18}\text{O}$ (A), $p\text{CO}_2$ (B), and silicate weathering flux (C). Abbreviations: ${}_{\text{bio}}\text{SiO}_2$ - biogenic silica; SWF – silicate weathering flux. Data sources indicated in the text.

4 Discussion

335

4.1 Implications for paleocirculation

The Blake Nose area is adjacent to the western margin of the North Atlantic subtropical gyre, which exerts a major control on nutrient availability in surface waters along the North American continental margin. Over the South



Atlantic Bight region, encompassing the Blake Plateau, the key mechanism fuelling modern phytoplankton production is sub-mesoscale frontal eddies arising from meanders on the landward side of the Gulf Stream System (GSS; Richardson, 2001; Gula et al., 2015). Comparable cyclonic eddies of <100 km diameter are observed also in other western boundary current (WBC) systems, which are generally viewed as oligotrophic settings (Roughan et al., 2017). These eddies are responsible for upward pumping of nutrients from sub-thermocline, nitrate-rich waters (Lee et al., 1991). Upwelled waters intrude onto the continental margin, and sustain rich biological production through the lifespan of an eddy (Roughan et al., 2017). Siliceous plankton production and export in the GSS is influenced by a number of factors, including Atlantic Meridional Overturning Circulation (AMOC) intensity, and the North Atlantic Oscillation, which together act to shift the GSS position relative to the North American seaboard on a decadal timescale (Sanchez-Franks and Zhang, 2015). Also the topography of the North American continental margin (Richardson, 2001) in conjunction with eustatic sea level variations exert a strong influence on the GSS path on long timescales, with features such as the Charleston Bump acting to deflect the jet trajectory toward the open ocean (Pinet et al., 1981; Gula et al., 2015).

A northeastward-flowing, wind- and Coriolis force-driven WBC likely operated in the North Atlantic at least since the Cretaceous (Gradstein and Sheridan, 1983), albeit at reduced strength relative to the modern before the final closure of the Central American Seaway (Montes et al., 2012). Given the overall stability of the western North Atlantic topography over the Cenozoic, occurrence of cyclonic frontal eddies were likely an inherent feature of the South Atlantic Bight region throughout the Paleocene and Eocene. The semi-periodic fluctuations in BN_{bioSiO_2} flux through time could therefore be also attributed to changes either in the mean GSS path (e.g., Wade and Kroon, 2002), or variations in sub-thermocline nutrient supply, which are largely dependent on vertical mixing of the ocean (Miskell et al., 1985; Moore et al., 2008) – or a combination of both processes.

Reconstructing intermediate- and deep-water circulation patterns in the North Atlantic through the early Cenozoic is more complex than reconstructing GSS history. Vahlenkamp et al. (2018) reviewed the existing perspectives on the Atlantic Ocean circulation through the Paleogene. ϵ_{Nd} reconstructions generally indicate a southern high-latitude source for the deep waters bathing the North American margin throughout the early-to-mid Paleogene (Thomas et al., 2003; Batenburg et al., 2018), although a Tethyan-sourced water mass is also hypothesized by some workers (Fontorbe et al., 2016; Vahlenkamp et al., 2018). At present, it is not known how a southern-sourced, northward-flowing deep water mass may have affected nutrient availability and upwelling in the western North Atlantic, especially along continental margins. The high diatom:radiolarian (D:R) ratios (Witkowski et al., 2020b, for further discussion see below) and common occurrence of well-preserved epiphytic diatoms such as *Arachnoidiscus* (see Witkowski et al., 2020a) suggest that much of BN_{bioSiO_2} fluxes through the Paleocene may be attributed to neritic production. Varying proportions of continental runoff-derived versus upwelled nutrient input could also be invoked to explain the disparity in bioSiO_2 fluxes between the more proximal Site 1051 and the more distal Site 1050 through the Paleocene.

An intensely debated question in the early Paleogene deep-water circulation reconstructions is the timing of the onset of NCW flow – a precursor to quasi-modern deep-water circulation (Via and Thomas, 2006). North Atlantic $\delta^{13}\text{C}$ records do not indicate major paleocirculation changes prior to the late Eocene (~38 Ma; Katz et al., 2011; Borrelli et al., 2014; Coxall et al., 2018), and numerous studies place the onset of AMOC either shortly prior to or following the EOT (Via and Thomas, 2006; Abelson and Erez, 2017; Coxall et al., 2018).

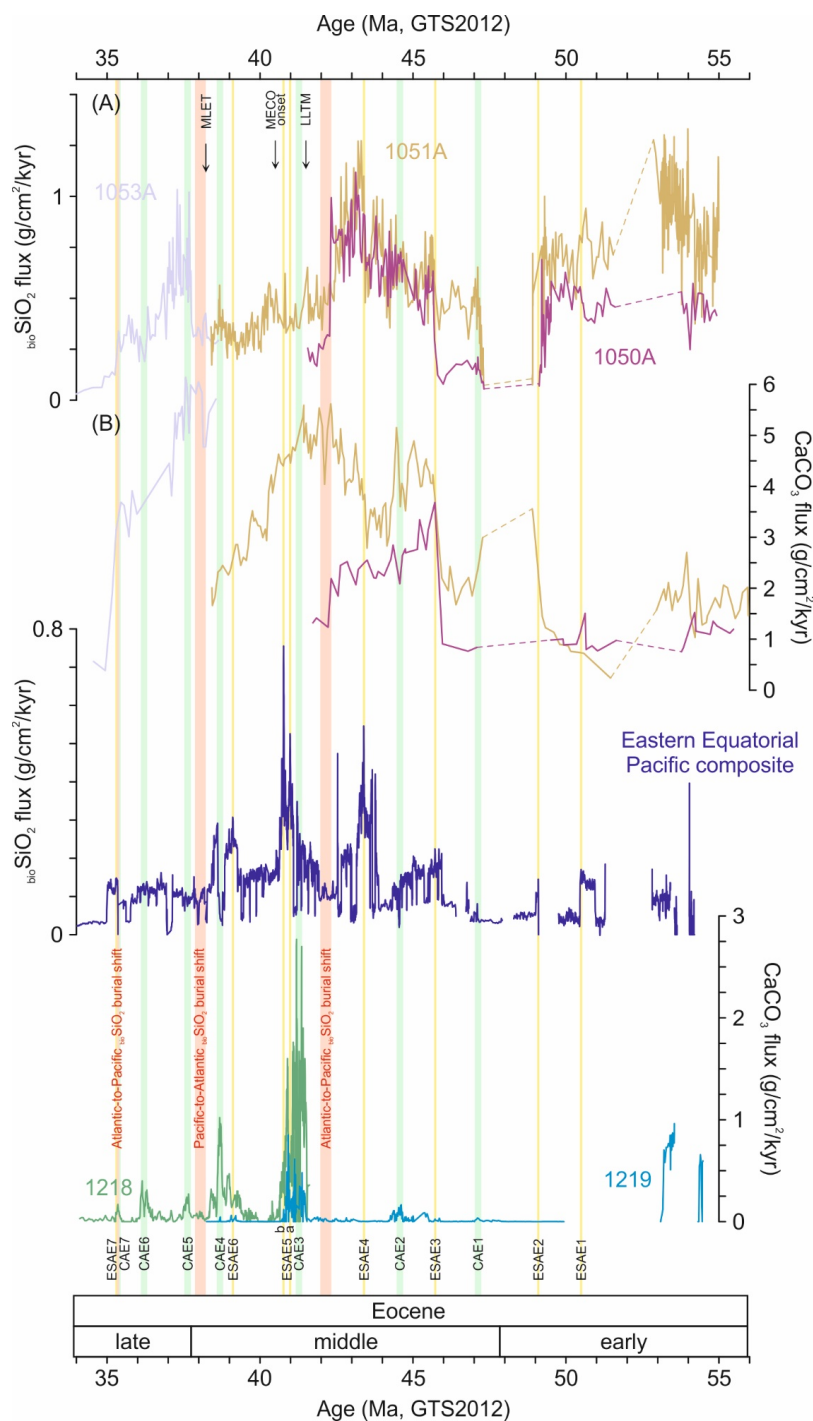


Figure 4. Eocene biogenic silica (A) and calcium carbonate (B) fluxes at Blake Nose sites plotted against biogenic silica (C) and calcium carbonate (D) fluxes at Eastern Equatorial Pacific sites. Blake Nose carbonate data from



380 Shipboard Scientific Party (1998c,d,f). Eastern Equatorial Pacific data from Moore et al. (2008) and Lyle et al. (2005).
Abbreviations: bioSiO_2 - biogenic silica; GTS2012 - Geologic Time Scale 2012, see Gradstein et al. (2012); MLET -
Middle-Late Eocene Turnover; LLTM - Late Lutetian Thermal Maximum; ESAE - Eocene Silica Accumulation Event;
CAE - Carbonate Accumulation Event.

385 In contrast to the timing of NCW flow initiation indicated by isotopic proxy records, the onset of widespread
drift deposition in the North Atlantic is documented much earlier, i.e., near the termination of the EECO (~49 Ma;
Hohbein et al., 2012; Boyle et al., 2017). This is also synchronous with ubiquitous deep-sea erosion coincident with the
EMET (Aubry, 1995; Witkowski et al., 2020b), strongly suggesting that the onset of vigorous northern-sourced bottom
current activity began at ~49–47 Ma (Vahlenkamp et al., 2018; Witkowski et al., 2020a). Following the EMET, the
390 northward-flowing GSS and the invigorated deep WBC facilitated diapycnal mixing, which likely enhanced biological
pump efficiency along continental margins of the western North Atlantic. This is consistent with a range of geochemical
proxies, including thallium isotope ($\epsilon^{205}\text{Tl}$) evidence for increased C_{org} burial from ~50 Ma (Nielsen et al., 2009) and
with surface-to-deep $\delta^{13}\text{C}$ gradients (Hilting et al., 2008). BN diatom assemblage data from Witkowski et al. (2020b)
also support an oligotrophic regime over Blake Nose for the time period prior to and including the EECO, based on high
395 percentages of hemiauloids. Following the EECO (after ~49 Ma), elevated percentages of diatom resting spores point to
alternating, perhaps seasonal, periods of nutrient enrichment and depletion, in line with strong periodic upwelling of
nutrients by means of Gulf Stream frontal eddies (Lee et al., 1991). This interpreted invigoration in ocean mixing led to
a considerable increase in primary production during the early middle Eocene, as evidenced by a rapid increase in both
 CaCO_3 and bioSiO_2 fluxes at BN at ~46 Ma (Fig. 4A,B).

400 4.2 Comparison to Eastern Equatorial Pacific bioSiO_2 flux records

The only published early Paleogene bioSiO_2 flux record from another region of comparable duration to the BN
composite record is that derived from Eastern Equatorial Pacific (EEP) cores (Moore et al., 2008). There are several
important differences between the Atlantic and Pacific records (Fig. 4), including (1) contrasting proportions of diatoms
in the BN versus EEP sediments; (2) the presence/absence of exported neritic material; and (3) a shorter time interval
405 covered by the EEP record (Eocene only). Where the records overlap in time, however, there is a variable degree of
coupling between bioSiO_2 flux records from BN and EEP.

High diatom:radiolarian (D:R) ratios in early-to-mid Paleogene sediments at BN were interpreted by
Witkowski et al. (2020b) to indicate that bioSiO_2 preserved was mostly of diatom origin. It is challenging, however, to
provide a quantitative estimate of diatom versus radiolarian contribution to total bioSiO_2 at BN, primarily because no
410 published diatom valve weight data are available. In the modern oceans, radiolarian tests are on average an order of
magnitude heavier than diatom valves (with differences in fact ranging over several orders of magnitude; Lisitzin,
1971). Assuming a 10:1 radiolarian to diatom skeleton weight ratio for the early Paleogene, and using an average
radiolarian test weight of 0.225 μg consistent with the range of values displayed by the oldest materials included in
Moore (1969), we make a rough estimate of diatom versus radiolarian contribution to total BN bioSiO_2 based on
415 quantitative siliceous microfossil counts of Witkowski et al. (2020b). As other siliceous plankton groups are sparse in
BN siliceous microfossil assemblages (Witkowski et al., 2020b), and likely contribute little bioSiO_2 to sediments
(Lisitzin, 1971), we exclude the relatively minor contributions of silicoflagellates, siliceous dinoflagellates, and



chrysophycean cysts from the calculations. These rough approximations indicate a mean diatom contribution of ~35.7% to the total biogenic silica content at BN (Fig. S6 in the online Supplementary Materials), with the highest values
420 observed for the early and middle Paleocene, consistent with the D:R ratios ranging as high as >200 reported by Witkowski et al. (2020b). Given that diatom valves are less resistant to dissolution than radiolarian tests, the contribution of diatoms to total bioSiO_2 in early Paleogene sediments at BN is likely underestimated due to selective dissolution. A final caveat on these considerations is that they disregard bioSiO_2 comprised in sponge spicules, for which no quantitative data are available from the BN cores.

425 In contrast, Moore et al. (2008) refer to the near-absence of diatoms in the early Paleogene EEP cores as an “enigma”. Although Moore et al. (2008) do not specify whether or not this observation is based on sieved residues, (thereby potentially missing diatom in the smaller sediment fractions), other Paleogene diatom reports from pelagic low-latitude Pacific sites corroborate this view (e.g., Fenner, 1984). We propose that the reason for this difference in diatom abundance in sediments between BN and EEP is twofold. Firstly, most early Paleogene diatom occurrences in
430 the Atlantic are in marginal settings (Witkowski et al., 2020b), where at least part of the preserved diatom assemblage may originate from offshore export of neritic plankton. Secondly, the radiolarian-rich Pacific sites mostly represent pelagic deposition at water depths of ~4–5 km. Diatom dissolution is facilitated by longer times in transit through the water column. Also, Al content, which is known to buffer diatom preservation in sediments (DeMaster, 2014), is lower in pelagic sediments relative to the continental margins. The BN and EEP records also differ in the magnitude of bioSiO_2
435 fluxes: as discussed in Witkowski et al. (2014; 2020b), the BN area received large volumes of neritic plankton through the early Paleogene, that underwent offshore export likely by means of frontal eddies, and the resultant bioSiO_2 fluxes are high. The pelagic EEP sites likely record only local, pelagic production and deposition, with low bioSiO_2 fluxes relative to the BN.

Eocene EEP sediment accumulation rates are generally low, punctuated by a series of elevated flux events
440 termed ESAEs (Eocene Silica Accumulation Events – see Moore et al., 2008) and CAEs (Carbonate Accumulation Events – see Lyle et al., 2005) (Fig. 4C-D). Between ~55 and 46 Ma, bioSiO_2 fluxes in the EEP are low, and appear decoupled from the BN records. ESAE 3 at ~45.8 Ma marks the onset of enhanced bioSiO_2 flux in the EEP (Fig. 4C). Notably, ESAE 3 appears to be age-equivalent to a prominent increase in BN bioSiO_2 and CaCO_3 fluxes (Fig. 4A vs C). ESAE 4 at ~44.3 Ma is correlative to the peak in middle Eocene bioSiO_2 flux at BN (Fig. 4A vs C). Following ESAE 4,
445 however, trends in bioSiO_2 flux again become decoupled between the two regions. bioSiO_2 fluxes diminish at BN between ~42 and 38 Ma, and a concomitant reduction is observed in the geographic distribution of siliceous microfossils in the Atlantic Ocean (Witkowski et al., 2020b) (Fig. 4A vs C). Thus, reduced bioSiO_2 accumulation between ~42 and 38 Ma is not a local phenomenon restricted to the BN area, but instead it is likely indicative of a major change in nutrient supply or paleocirculation that affected the entire Atlantic basin. In contrast, this late middle Eocene
450 period of low bioSiO_2 flux at BN precisely corresponds to an interval of elevated bioSiO_2 fluxes in the EEP (Fig. 4A vs C), including the bimodal ESAE 5, which represents the peak in the Eocene EEP bioSiO_2 accumulation at ~41 Ma.

Near the end of the middle Eocene, ESAE 6 is abruptly terminated at ~38.5 Ma, concomitant with a major radiolarian turnover at EEP sites (Moore et al., 2008). A similar episode of accelerated turnover in radiolarians has been identified at ~38.25 at BN (Kamikuri and Wade, 2012; Newsam et al., 2017), but in conjunction with a rapid rise in
455 bioSiO_2 flux levels. ESAEs 7 and 8 in the EEP are minor events at ~35 and ~34 Ma, respectively, and no age-equivalent events are observed in the BN bioSiO_2 flux record. We interpret the decoupling between BN and EEP bioSiO_2 flux



records after ~42 Ma as a series of inter-basin bioSiO_2 accumulation shifts (Fig. 4A vs C), likely associated with deep-water circulation changes (Berger, 1970) affecting the seabed preservation of bioSiO_2 .

460 Diminished BN bioSiO_2 fluxes indicate lower nutrient supply from ~42 to 38 Ma, i.e., through the interval spanning both Late Lutetian Thermal Maximum (LLTM, ~41.5 Ma; Westerhold et al., 2018b) and Middle Eocene Climatic Optimum (MECO, ~40 Ma; Bohaty et al., 2009; Henehan et al., 2020). Modern field observations indicate that diminished supply of nutrients to the GSS may result from weakened AMOC. Witkowski et al. (2020b) demonstrate a reduced geographic range of biosiliceous accumulation in the Atlantic between ~42 and 38 Ma, which is also consistent with a diminished nutrient supply. Accordingly, we propose a period of potentially weakened AMOC spanning both the
465 LLTM and MECO events.

The Pacific-to-Atlantic bioSiO_2 flux shift at ~38 Ma coincides with increased rates of radiolarian turnover and planktonic foraminiferal extinction designated MLET by Kamikuri and Wade (2012). More importantly, however, the abrupt increase in bioSiO_2 flux at Site 1053 took place in conjunction with shifts in benthic foraminiferal $\delta^{13}\text{C}$ (Katz et al., 2011; Borrelli et al., 2014; Coxall et al., 2018) interpreted to mark the onset of NCW export.

470 Thus, the repeated shifts in bioSiO_2 fluxes between NW Atlantic and EEP through the late middle and late Eocene suggest that the ‘lagoonal’ Atlantic (=carbonate burial-favoring) versus ‘estuarine’ Pacific (=SiO₂ burial-favoring) circulation pattern proposed by Berger (1970) was established in the lead-up to LLTM and temporarily reversed at the MLET before its final reestablishment shortly before the EOT. These shifts were likely driven by changes in deep-sea circulation patterns. Importantly, however, this interpretation implies that the two scenarios for
475 NCW export inception (at EOT: Borrelli et al., 2014; and Coxall et al., 2018; versus at the end of the EECO: Hohbein et al., 2012; Boyle et al., 2017; and Vahlenkamp et al., 2018) are not mutually exclusive. The patterns in Atlantic to Pacific bioSiO_2 flux fractionation outlined above suggest a ~4 myr period of the early AMOC disruption spanning the last of the Eocene greenhouse warming events, i.e., LLTM and MECO. Moreover, the evidence supporting NCW inception in the late Eocene or early Oligocene may in fact point to a reinvigoration of AMOC flow following a period
480 of weakened overturning circulation between 42 and 38 Ma.

4.3 Implications for the silicate weathering feedback operation mode

The silicate weathering feedback has been proposed as the key mechanism for keeping the Earth surface temperatures within a habitable range over 10^5 – 10^6 yr-timescales (Walker et al., 1981; Kasting, 2019). By consuming
485 atmospheric CO₂ and releasing alkalinity and dissolved silicon (Penman, 2016), this feedback mechanism also influences key biogeochemical cycles within the ocean–atmosphere system, resulting in a tight coupling between the marine carbon and silicon cycles (Tréguer and De La Rocha, 2013). In recent years, however, the operation of the silicate weathering feedback through the Cenozoic has been disputed, with a special focus on whether the strength of the link between climate and continental weathering varies through time (Caves et al., 2016; van der Ploeg et al., 2018). One point of disagreement concerns the early Paleogene. In the traditional view (hereafter “constant feedback strength
490 scenario”), which assumes a linear relationship between global temperature change and weathering, the early Paleogene greenhouse climates should facilitate increased rates of chemical weathering on land directly proportional to the magnitude of CO₂-driven warming (e.g., Misra and Froelich, 2012; Sluijs et al., 2013; Penman, 2016). An emerging alternative view (hereafter “variable feedback strength scenario”) is that during the Eocene the feedback strength was at a minimum level (Caves et al., 2016; van der Ploeg et al., 2018), with lowered silicate weathering intensity (and, hence,



495 reduced weathering feedback strength) promoting high $p\text{CO}_2$ levels and a warm climate (Misra and Froelich, 2012).
Assuming that the early-to-mid Paleogene silicon cycle already operated in its present-day form (Fontorbe et al., 2016;
Conley et al., 2017), these scenarios should lead to different marine bioSiO_2 flux responses. In the constant feedback
strength scenario, bioSiO_2 production and burial would be expected to peak during the EECO, i.e., the warmest period of
the Cenozoic era (e.g., Kirtland-Turner et al., 2014; Cramwinckel et al., 2018; Westerhold et al., 2018a). In the variable
500 feedback strength scenario, the silicate weathering flux should decrease through the Eocene (Caves et al., 2016), leading
to a decrease in dissolved silicon supply and bioSiO_2 burial.

In the BN composite, both % bioSiO_2 and bioSiO_2 flux values are high in the lead-up to the EECO (~55 through
53.5 Ma) and considerably lower in the final phases of the EECO (~51 through 49 Ma). The hiatus spanning ~53.5
through 52 Ma, however, precludes any definitive conclusions on the behavior of the silicate weathering feedback
505 through the entire EECO period, particularly with regard to the constant versus variable strength of its link to climate.
Importantly, however, bioSiO_2 flux values through the middle Eocene are consistently higher than background
Paleocene–early Eocene values both in the Atlantic and in the Pacific (see also Moore et al., 2008, and Section 4.2),
which cannot be easily reconciled with the linear feedback strength scenario. Thus, it appears that long-term trends in
 bioSiO_2 flux are more consistent with the variable feedback strength scenario, suggesting that the strength of the link
510 between climate and terrestrial silicate weathering may indeed be variable through time. Secondly, the high levels of
 bioSiO_2 flux through the middle Eocene cooling (Fig. 2B) point to enhanced nutrient supply from invigorated ocean
circulation as a major control on bioSiO_2 flux in the younger part of our study period.

5 Conclusions

Deep-water temperatures, atmospheric greenhouse gas levels, and continental weathering are identified as the
515 main drivers of bioSiO_2 flux through the Paleocene and Eocene at Blake Nose in the western North Atlantic Ocean.
Variations in bioSiO_2 fluxes support an early export of NCW, but also suggest a period of disruption to the early form of
AMOC between ~42 and 38 Ma, as suggested by the Atlantic to Pacific bioSiO_2 flux fractionation. Additionally, BN
 bioSiO_2 fluxes indicate that the long-term behavior of the silicate weathering thermostat conforms to the variable rather
than constant weathering–climate feedback strength scenario.

520 **Code/data availability:** all data generated in this study is included in the online Supplementary Materials.

Competing interests: The authors declare that they have no conflict of interest.

Author contribution: JW, SMB and DEP designed the study. JW, KB, BSW EM performed sampling and analyses.
EM performed the statistical analysis. All authors participated in interpreting the data. JW prepared the manuscript, with
input from all co-authors.

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