

A global ocean opal ballasting-silica relationship

B. B. Cael¹, Mark Moore², Colleen B. Mouw³, Chris Bowler⁴, Edward Mawji¹, Stephanie Anne Henson¹, Corinne Le Quéré⁵, Tereza Jarníková⁶, and Joe Guest⁶

¹National Oceanography Centre

²University of Southampton

³University of Rhode Island

⁴Institut de biologie de l'Ecole normale supérieure (IBENS), Ecole normale supérieure, CNRS, INSERM, PSL Université Paris 75005 Paris, France.

⁵School of Environmental Sciences, University of East Anglia, UK

⁶University of East Anglia

August 4, 2023

Abstract

Opal and calcium carbonate are thought to regulate the biological pump's transfer of organic carbon to the deep ocean. A global sediment trap database exhibits large regional variations in the organic carbon flux associated with opal flux. These variations are well-explained by upper ocean silica concentrations, with high opal 'ballasting' in the silica-deplete tropical Atlantic Ocean, and low ballasting in the silica-rich Southern Ocean. A plausible, testable hypothesis is that opal ballasting is due to mineral protection, and varies because diatoms grow thicker frustules where silica concentrations are higher, protecting less organic carbon per unit opal. These patterns do not emerge in an advanced ocean biogeochemical model when opal ballasting is represented using a single global parameterization for diatoms, indicating the need for additional parameterization of the dependence of diatoms traits on silica concentration to capture the links between elemental cycles and future changes in the biological pump.

A global ocean opal ballasting–silica relationship

B. B. Cael¹, C. Mark Moore², Joe Guest³, Tereza Jarníková³, Colleen B. Mouw⁴, Chris Bowler^{5,6}, Edward Mawji¹, Stephanie A. Henson¹, and Corinne Le Quéré³

¹National Oceanography Centre, Southampton, UK

²School of Ocean and Earth Science, University of Southampton, UK

³School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, UK

⁴University of Rhode Island, Graduate School of Oceanography, Narragansett, RI, USA

⁵Institut de Biologie de l'Ecole Normale Supérieure (IBENS), Ecole Normale Supérieure, CNRS,

INSERM, Université PSL, 75005 Paris, France

⁶Stazione Zoologica Anton Dohrn, Naples, Italy

Key Points:

- Opal ballasting (particulate organic carbon flux per opal flux) varies 6-fold across ocean regions; calcium carbonate ballasting is uniform.
- Silica concentration predicts opal ballasting which suggests that the latter occurs via mineral protection and varies with diatom frustule thickness.
- This ballasting pattern's absence from a sophisticated biogeochemical model indicates the need for a novel mechanistic parameterization.

Corresponding author: B. B. Cael, cael@noc.ac.uk

Abstract

Opal and calcium carbonate are thought to regulate the biological pump's transfer of organic carbon to the deep ocean. A global sediment trap database exhibits large regional variations in the organic carbon flux associated with opal flux. These variations are well-explained by upper ocean silica concentrations, with high opal 'ballasting' in the silica-deplete tropical Atlantic Ocean, and low ballasting in the silica-rich Southern Ocean. A plausible, testable hypothesis is that opal ballasting is due to mineral protection, and varies because diatoms grow thicker frustules where silica concentrations are higher, protecting less organic carbon per unit opal. These patterns do not emerge in an advanced ocean biogeochemical model when opal ballasting is represented using a single global parameterization for diatoms, indicating the need for additional parameterization of the dependence of diatoms traits on silica concentration to capture the links between elemental cycles and future changes in the biological pump.

Plain Language Summary

Opal, or hydrated silica, is taken up in the surface ocean by diatoms, which use it to construct their protective frustules. Another type of plankton, coccolithophores, generate protective platelets from calcium carbonate. These two minerals, and thereby plankton types, play major roles in the cycling of carbon globally. The 'biological carbon pump' transfers carbon from the atmosphere to the ocean's depths, where it can stay for centuries to millennia. This process has influenced past atmospheric carbon dioxide concentrations and could also influence future carbon dioxide concentrations and hence climate. The transfer of carbon to the deep ocean is known to be partially regulated by the amount of 'ballast' minerals in sinking particles, especially opal and calcium carbonate, which are denser and cause particles to sink faster and/or protect organic carbon from microbial consumption. Here we show that unlike calcium carbonate, the ballasting effect of opal varies a great deal between different regions of the ocean. The variation in opal ballasting is well-explained by the upper-ocean concentration of silica in these regions. This suggests a simple explanation: when silica concentrations are high/low, diatoms grow thick/thin frustules. Including this process in carbon cycle models may improve their ability to predict future biogeochemical cycles and climate.

1 Introduction

The biological carbon pump (BCP) entails the uptake, processing and transfer of organic carbon to the deep ocean by biological processes. Without the BCP, atmospheric CO₂ levels would be ~200 ppm higher than they currently are (Parekh et al., 2006; Kwon et al., 2009). Particulate organic carbon (POC) and associated nutrients sinking out of the ocean's upper layer are gradually remineralized by grazing processes and microbial activity. The depth at which POC is remineralized determines the water mass that the resulting inorganic carbon enters, and thus the timescales of potential re-exchange with the atmosphere. Generally, the deeper POC can penetrate into the ocean, the longer it is stored (Siegel et al., 2021; Baker et al., 2022). However, the mechanistic processes that underlie the considerable spatial and temporal variability in POC flux and remineralization (Cram et al., 2018; Bol et al., 2018) are still debated (Henson et al., 2022). One hypothesis posits that a portion of sinking POC is associated with 'ballast minerals', i.e. calcium carbonate and biogenic silica generated by calcifying organisms and diatoms, respectively (Armstrong et al., 2001; Klaas & Archer, 2002). These are thought to deepen the remineralization depth of POC either through protection of the POC, or by increasing the particles' excess density and thus sinking speed. Although the presence of ballast minerals has a strong statistical relationship with remineralization depth, a lack of mechanistic understanding introduces challenges for parameterising ballasting in Earth

system models, despite its potential to be an important component of carbon cycle-climate feedbacks (Barker et al., 2003; Petrou et al., 2019; Heinze et al., 2019).

Our objectives here are to diagnose i) the ballast effects of opal and calcium carbonate (in terms of the POC flux at a reference depth associated with a unit of opal or calcium carbonate flux), ii) the extent to which the ballasting effects vary among ocean regions, iii) the drivers of regional variations, and iv) the need to introduce new parameterizations in global ocean biogeochemical models. To achieve these objectives, we apply a statistical model based on the robust log-normality of ocean particle fluxes (Cael et al., 2018, 2021) to a global sediment trap database (Mouw et al., 2016). We find that, while the majority of parameters of the statistical model remain fairly constant, the ballasting by opal varies by almost an order of magnitude between different large regions. We discuss various possible mechanisms to explain this regional difference but identify one that is most parsimonious and plausible based on upper ocean silica availability and diatom frustule thickness, which constitutes a hypothesis that is experimentally testable. We show that this relationship does not occur in a state-of-the-art ocean biogeochemical model (Buitenhuis et al., 2019), underscoring that the opal ballasting pattern that we uncover here is produced by a currently unparameterized process. We then develop an easily implementable parameterization for opal ballasting based on silica concentration.

2 Methods

2.1 Statistical Model

Following (Cael et al., 2018, 2021), our statistical model is derived from treatment of particle flux variability as log-normal. This is based on the empirically validated (Cael et al., 2018, 2021; Cael, 2021) argument that i) net primary production varies log-normally because multiple conditions need to be met in order for production to occur, such that the ‘law of necessary conditions’ applies, ii) particle export out of the euphotic layer is equal to net primary production times export efficiency by definition, and export efficiency is a variable quantity, and iii) particle flux at a given depth is equal to particle export times the transfer efficiency to that depth, which is also a variable quantity. If the fluxes of particulate organic carbon ($\mathcal{F}_{OC}$ ($\text{mg C m}^{-2} \text{ d}^{-1}$), particulate inorganic carbon ($\mathcal{F}_{IC}$ ($\text{mg C m}^{-2} \text{ d}^{-1}$, i.e. calcium carbonate in units of C mass), and particulate silica ($\mathcal{F}_{Si}$ ($\text{mg S m}^{-2} \text{ d}^{-1}$, i.e. opal in units of S mass), are log-normally distributed (Cael et al., 2021), and the latter both act in concert as ballasting minerals (i.e. organic carbon flux to a given depth can be facilitated by either or both minerals and does not necessarily require both), then they should be related by an equation of the form (Campbell, 1995)

$$\mathcal{F}_{OC} = (\alpha_{IC}\mathcal{F}_{IC} + \alpha_{Si}\mathcal{F}_{Si})^\gamma z^{\Delta b} \quad (1)$$

where α_{IC} (dimensionless) is the flux of organic carbon associated with a unit of inorganic carbon, α_{Si} (g C/g Si) is the flux of organic carbon associated with a unit of silica, γ (dimensionless) is the degree of sub-/super-linearity in the scaling relationship between organic carbon fluxes and ballast mineral fluxes, and Δb is the difference in the vertical attenuation (using a power-law approximation (Martin et al., 1987)) of organic carbon flux versus ballast mineral flux. Here z is normalized to a given reference depth z_o , for which we use 1km. Our results are not affected by this choice. Hence Δb encodes the extent to which organic carbon flux attenuates with depth to z_o , i.e. 1km, compared to ballast mineral flux. γ can be interpreted as the extent to which the effect of ballast minerals have ‘diminishing returns’ because if $\gamma < 1$ and increasingly so as $\gamma \rightarrow 0$, particles with e.g. twice the ballast mineral loading will have less than twice the organic carbon content (γ can in principle be > 1 but this is mechanistically implausible and is not

seen in the observations). α_{IC} and α_{Si} can be interpreted as the organic carbon flux per unit of each ballast mineral flux at the reference depth; strictly speaking this is only true when $\gamma = 1$, but regardless of the value of γ the ratio of the α values captures the relative ballast effect per unit mass of each mineral. (Note that Equation 1 is equivalent to the one given in (Cael et al., 2021), with Δb used here in replacement of b to make it explicit that this parameter captures the *difference* in vertical attenuation of organic carbon versus ballast mineral fluxes, $\alpha_{IC} = \kappa^{1/\gamma}$ and $\alpha_{Si} = \beta\kappa^{1/\gamma}$ used in replacement of κ and β to make the ballast effect of each mineral explicit parameters, and a reference depth of 1km used rather than 3500m because measurements of the full water column are considered rather than just near-bottom sediment traps.)

2.2 Sediment Trap Data

We utilized a global dataset of POC, PIC, and particulate silica (PSi) flux estimated from POC, PIC, and PSi concentration observations from sediment traps (Mouw et al., 2016). The database also includes ^{234}Th -based POC fluxes and the fluxes of other elements and molecules, but we only analyze coincident POC, PIC, and PSi flux measurements from sediment traps. Data were compiled from public repositories and directly from the literature. When CaCO_3 fluxes were reported and PIC fluxes were not, the former were converted to the latter using the ratio of their molar masses; the same was done for SiO_2 and Si(OH)_4 to PSi fluxes. The data set contains 15,792 individual POC flux estimates, measured on timescales of days to weeks, at 674 unique locations collected between 1976 and 2012. 85% of the observations are concentrated in the Northern Hemisphere. Most of the dataset (71%) was measured at $\geq 500\text{m}$, with the most common deployment depths between 1000–1500 m.

These data are split into five broad geographic regions. The Southern Ocean (SO) is defined here as all data poleward of 30°S ; the North Pacific (NP) and Atlantic (NA) are defined as all data poleward of 30°N in each basin; the Tropical Pacific (TP) and Atlantic (TA) are defined as all data equatorward of 30° in each basin. (There are few measurements in the Indian Ocean.) The data from major time-series sites were excluded from our analyses, as the database is unavoidably very spatially biased even without including these sites, and these locations would be vastly over-represented if included, such that our global analysis would be largely dictated by the behavior of a few locations (the majority with low silica concentrations, furthermore). Excluding these locations, the database includes 768/2274/2286/1327/504 co-located measurements of $\mathcal{F}_{OC}$, $\mathcal{F}_{IC}$, and $\mathcal{F}_{Si}$ in the SO/NP/TP/NA/TA respectively.

2.3 Statistical Analysis

Equation 1 is then fit to the data from each region following the procedure in (Cael et al., 2021). The $(\alpha_{Si}/\alpha_{IC}, \Delta b)$ that yields the best fit regression, using a scaling relationship of the form $y \propto x^\gamma$, between $\mathcal{F}_{OC}z^{\Delta b}$ and $\mathcal{F}_{IC} + \frac{\alpha_{Si}}{\alpha_{IC}}\mathcal{F}_{Si}$ is identified. Major axis type II regression is used to account for the fact that uncertainties exist on both the x - and y -axis. Multiplicative (i.e., % rather than absolute) errors are assumed, consistent with these variables scaling with one another and being log-normally distributed. Parameter uncertainties are calculated via bootstrap resampling (Efron & Tibshirani, 1986) with 1,000 bootstrap reiterations.

Equation 1 can be inverted to estimate the opal ballasting α_{Si} for each individual measurement. This can be done by taking the measured fluxes of OC, IC, and Si and the measurement depth, along with a representative global value for γ , Δb , and α_{IC} (here we use the mean across regions as these other parameters are fairly constant between regions, see §3), and rearranging Equation 1 to yield

$$\alpha_{Si} = \frac{1}{\mathcal{F}_{Si}} \left((\mathcal{F}_{OC} z^{-\Delta b})^{1/\gamma} - \alpha_{IC} \mathcal{F}_{IC} \right) \quad (2)$$

This estimate of α_{Si} is then compared to co-located upper ocean silica concentrations ($[\text{Si}]$, ($\mu\text{mol/kg}$)) to test the hypothesis that higher $[\text{Si}]$ values are associated with lower α_{Si} values. $[\text{Si}]$ values were taken from the World Ocean Atlas 2018 (Garcia et al., 2019). The 80m depth at which $[\text{Si}]$ is considered here was selected as the depth at which the Spearman rank correlation between $[\text{Si}]$ at that depth and the inferred α_{Si} at the same latitude and longitude is a maximum. For 80m, the correlation is 0.68. Our results are not sensitive to this choice; the correlation for all depths 0-500m is ≥ 0.65 . The logarithm of α_{Si} is then regressed against the logarithm of $[\text{Si}]$ (at 80m) using the second-order polynomial of the form $y = p_2 x^2 + p_0$, to capture heuristically that α_{Si} asymptotes to a constant value as $[\text{Si}] \rightarrow 0$. Adding the term $p_1 x$ yielded no difference as the p_1 term was not significantly different from zero.

2.4 Numerical Model

A global ocean biogeochemical model is used to explore if the properties inferred using the database emerge in the current generation of models. We use the NEMO-PlankTOM12 model which represents explicitly twelve Plankton Functional Types (PFTs), six phytoplankton types (picophytoplankton, N_2 -fixers, diatoms, *Phaeocystis*, and other mixed-phytoplankton), five zooplankton (protozooplankton, mesozooplankton, crustacean and gelatinous macrozooplankton, and pteropods) and bacteria (Buitenhuis et al., 2019; Le Quéré et al., 2016; Wright et al., 2021). All PFTs are represented using vital parameters of growth and loss rates based on available observations, and interact with each other using food preferences generally based on size. Growth rates are based on temperature and vary with nutrient availability. The model includes a full silicate cycle, with its dissolved, biogenic (with a fixed Si:C ratio for diatoms) and detrital pools. Sinking of organic matter is a function of the ballasting density of the particles. Full equations are presented in the supplementary of (Le Quéré et al., 2016), with additional parameterization of calcium carbonate as in (Buitenhuis et al., 2019). The model is embedded in the NEMOv3.6 general ocean circulation model, and is forced with NCEP reanalysis data. Compared to its last published version described in (Friedlingstein et al., 2022), the model introduces a simple sediment model which stores material from sinking fluxes in an additional bottom layer. To maintain mass balance, nutrients are removed from the sediment layer to equalize the river and dust fluxes. The model also includes further optimization of global parameters to reproduce the size and vertical profiles of the observed organic carbon, silica and calcium carbonate sinking rates presented here.

3 Results & Discussion

3.1 Regional Scaling Relationships

Figure 1 shows the fit of Equation 1 to the sediment trap data in each region. In each case, $\mathcal{F}_{OC}$ is well-predicted from ballast fluxes, with $r^2 = 0.70 - 0.81$. The parameters α_{IC} , γ , and Δb vary little between regions, with coefficients of variation of 10%, 6%, and 24% respectively (these parameters are discussed below). By contrast, the ballast effect of opal, α_{Si} , has a coefficient of variation of 77%, and varies by more than 6-fold between regions from a value of 1.3 ± 0.2 g C/g Si in the Tropical Atlantic to a value of 0.20 ± 0.02 g C/g Si in the Southern Ocean. In other words, in the Tropical Atlantic 1 mg Si $\text{m}^{-2} \text{d}^{-1}$ of opal flux is associated with more than six times more organic carbon flux at 1km than 1 mg Si $\text{m}^{-2} \text{d}^{-1}$ of opal flux in the Southern Ocean. The highest α_{Si} values are found in the Atlantic, then the Pacific and then the Southern Ocean, and within the Atlantic and Pacific Oceans, the tropical regions have larger α_{Si} values than the Northern regions (Figure 1f). Altogether there appears to be a very large dif-

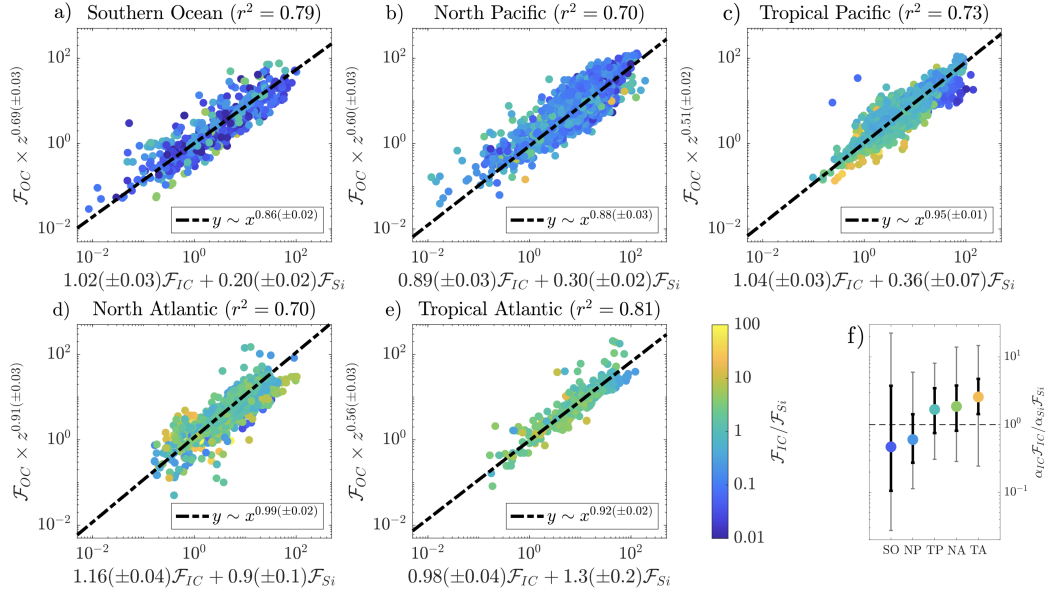


Figure 1. a-e) Scaling relationships corresponding to Equation 1 between organic carbon and ballast fluxes for different large regions. Color indicates ratio of fluxes of different ballast minerals. Parameter estimates are given on x- and y-axis labels. Units on both axes are $\text{mg C m}^{-2} \text{d}^{-1}$. Parameter values and uncertainties are estimated as described in the Methods. f) Median, interquartile range, and 95% range of ratio of POC flux at 1km estimated to be associated with inorganic carbon vs. opal (i.e. $\alpha_{IC}\mathcal{F}_{IC}/\alpha_{Si}\mathcal{F}_{Si}$) for each region. Dashed black line corresponds to equal organic carbon flux associated with each ballast mineral.

ference in the Si associated mineral ballasting between different ocean regions, with potentially large implications for ocean biogeochemical cycling.

Despite the much smaller α_{Si} values in the Southern Ocean and North Pacific, the far larger $\mathcal{F}_{Si}$ fluxes in these regions also mean that opal is associated with more POC flux at 1km than inorganic carbon for a majority of measurements in those regions (Figure 1f), captured by the ratio $\alpha_{IC}\mathcal{F}_{IC}/\alpha_{Si}\mathcal{F}_{Si}$. In the other three regions, calcium carbonate is associated with more POC flux at 1km, i.e. $\alpha_{IC}\mathcal{F}_{IC} > \alpha_{Si}\mathcal{F}_{Si}$, for a majority of measurements, as has often been reported in the literature (Klaas & Archer, 2002; Francois et al., 2002; Armstrong et al., 2001; Wilson et al., 2012). The large variability of this ratio between measurements in all regions, however, underscores that both ballast minerals play important roles; the interquartile range of $\alpha_{IC}\mathcal{F}_{IC}/\alpha_{Si}\mathcal{F}_{Si}$ spans values from <1 to >1 for all regions besides the tropical Pacific. (Note that this ratio is insensitive to whether molar or mass units are used.)

Parameters other than α_{Si} are fairly uniform across regions and change in plausible ways in light of the processes controlling the biological pump. α_{IC} is nearly constant between regions, consistent with PIC either increasing particles' excess density or protecting POC similarly between regions. γ is slightly <1 in all regions except the North Atlantic, but only slightly so, indicating some degree of 'diminishing returns' on the effect of ballast minerals, but not enough to make as large a difference to POC fluxes as variations in α_{Si} . Δb is higher at higher latitudes, consistent with some sediment-trap derived patterns for b (Henson et al., 2012), though other studies find the opposite pattern (Marsay et al., 2015). Note that we do not find systematic behavior with depth in the residuals, which suggests that a power-law approximation of flux attenuation with

depth is suitable for our analysis. We do not consider the variations in these parameters further.

3.2 Possible Mechanisms

A simple and arguably parsimonious explanation for the regional variations in α_{Si} is that variations in α_{Si} are determined by upper ocean silica concentrations ($[Si]$, $\mu\text{mol/kg}$). Indeed, $[Si]$ is lowest in the surface waters of the Atlantic and highest in the Southern Ocean, due to the interaction of the meridional overturning circulation with both the temperature dependent long remineralization length scale of Si and high Si:N uptake ratios in the surface Southern Ocean (Sarmiento et al., 2007, 2004; Holzer et al., 2014; Gnanadesikan, 1999). Globally Si is largely trapped in the Southern Ocean (Holzer et al., 2014) where ventilation of Si-rich deep waters is coupled to high production and export of P_{Si} which is largely remineralized at depths below the northward flowing Antarctic intermediate and sub-Antarctic mode waters (AAIW/SAMW) (Sarmiento et al., 2007). Outside the Southern Ocean, the Atlantic is filled by the upper branch of the overturning circulation, which is ventilated by AAIW/SAMW formed within the relatively Si-depleted lower latitudes of the Southern Ocean (Sarmiento et al., 2004), while the Pacific is filled more by the lower branch, which is ventilated by the relatively Si-rich higher latitudes in the Southern Ocean. Furthermore, tropical regions in the Atlantic and Pacific are more Si-depleted than their Northern counterparts because some ventilation of deep waters occurs at high latitudes, even in the Pacific (Qiu & Huang, 1995). As a result, Atlantic diatoms grow in the most Si-depleted conditions and Southern Ocean diatoms grow in the most Si-replete conditions, with tropical diatoms growing in intermediate Si concentrations. The more Si-deplete the conditions in which diatoms grow, the less opportunity diatoms have to meet or exceed their minimum quota of silica. This will tend to lead to lower Si:C stoichiometry for diatoms in more Si-deplete conditions, meaning thinner-frustuled diatoms of a given size and/or larger diatoms (because silica is predominantly contained in diatoms' frustules, whereas carbon is predominantly contained in diatoms' interiors). If opal ballasting is due to protection of organic carbon by intact diatom frustules rather than a particle-density-driven effect, then thinner or larger frustules will correspond to more protection of organic carbon per unit opal, and hence larger α_{Si} . (In general, large variations in α_{Si} between regions are consistent with a mineral protection mechanism rather than a particle density mechanism for ballasting; opal's chemical characteristics do not vary by region, so the extent to which its inclusion in particles affects their density and thereby sinking speed should not be expected to vary regionally.) Diatoms in the Southern Ocean, and to a lesser extent in the (North) Subarctic Pacific, will thus be expected to have more ability to make thicker frustules in order to protect themselves from grazers, as observed (Assmy et al., 2013; Pančić et al., 2019), which results in higher Si:C ratios and lower α_{Si} values. We thus hypothesize that there should be a negative relationship between α_{Si} and $[Si]$ (see §3.3).

Several other factors may complicate this simple explanation for regional variation in α_{Si} . Different diatom taxa are characterized by different morphologies with widely varying sizes and silica frustule pattern variations (Round et al., 1990). Different diatom species also exhibit specific biogeographies, inhabiting different ocean regions (Tréguer et al., 2018; Malviya et al., 2016). Sporulation of diatoms, especially of those abundant in the Southern Ocean such as *Chaetoceros*, may also influence the Si:C of organic material sinking into the deep sea (Armand et al., 2008). The different compositions of diatom communities in different oceanic regions will therefore impact opal ballasting, but may in turn be influenced by the global availability of Si (Figure 2b). Furthermore, the Si content of diatom frustules can be impacted by environmental conditions other than $[Si]$. Silicification of diatoms is tightly linked to the cell cycle of growth, with Si uptake primarily occurring during the G2 interphase (Martin-Jézéquel et al., 2000). If the availability of other nutrients needed for cell growth (nitrate, phosphate, or iron) or other external growth conditions slow or prolong the G2 phase of the cell cycle in diatoms, sili-

cification and diatom ballast increases. It has also been reported that increased grazing pressure may also lead to more heavily silicified diatoms (Pondaven et al., 2007) presumably as a mechanism for organisms to enhance their protection from grazing losses. In contrast, Si deficiency is the only condition that acts to reliably lower the silica content of the diatom cell wall (Brzezinski et al., 1990). All these factors are likely to impact the formation and degradation of particles. Fecal pellets can also contribute appreciably to POC fluxes and their stoichiometry is necessarily reflective of their prey (Ducklow et al., 2001), so the selective grazing of diatoms of different frustule thicknesses (Ryderheim et al., 2022) and the relative balance of fecal pellets and aggregates in total POC fluxes will also play a role. Additionally, dust deposition is known to vary between regions and may further affect particles directly by being incorporated as lithogenic ballast (n.b. these are not collated in the (Mouw et al., 2016) database) or indirectly by supplying nutrients such as iron and thereby influencing phytoplankton communities.

3.3 Silica–Opal Ballasting Relationship

To test for a relationship between α_{Si} and [Si] more quantitatively, we use Equation 2 to estimate α_{Si} for each sediment trap measurement. For (α_{IC} , Δb and γ) we use the means over the five regions (= 1.02, 0.65, 0.92 respectively). Our results are not sensitive to these parameter values. We then compare these estimates to the co-located [Si] (at 80m depth). Figure 2a shows that the estimated α_{Si} decreased from a value of ~ 1.8 when [Si] $\rightarrow 0$, to small values as [Si] becomes large. This relationship is approximately described by the function $\alpha_{Si} = 1.8e^{-0.2\ln[Si]^2}$ ($r^2 = 0.49$, $p \ll 0.01$). Decreasing α_{Si} with increasing [Si] is consistent with the hypothesis presented above, as low-[Si] regions would correspond to thinner diatom frustules and more protected organic carbon per unit [Si], and the opposite for high-[Si] regions.

3.4 Model Simulation

To test for whether the observed [Si]- α_{Si} relationship is found in a numerical model’s historical simulation that does not parameterize the proposed frustule thickness mechanism, we sample the model analogously to how the real ocean has been sampled and repeat the same analysis on the pseudo-observations. Specifically, we draw $\mathcal{F}_{OC/IC/Si}$ values at the same latitudes, longitudes, depths, and months for which we have sediment trap measurements from monthly model output, using a randomly selected model year, 2000. Neither sub-monthly nor interannual variations should affect the relationship we investigate here. We also draw corresponding [Si] values at 80m depth. We then repeat the analysis from §2.3 on these data. We use the observational regional means of (α_{IC} , Δb and γ) as in §3.3. Our results are not affected by using the regional means for model pseudo-observations or using parameter combinations from specific observed or modeled regions.

We find a negative but far weaker relationship between model [Si] and inferred α_{Si} , with a correlation coefficient of -0.18 (compared to -0.67 for the observations). For a relationship of the form $y = p_2x^2 + p_0$ as fit to the observations above, the r^2 is 0.05 with $p_2 = +0.067 \pm 0.004$, compared to $r^2 = 0.49$ with $p_2 = -0.202 \pm 0.003$ for the observations. Thus the observed strong negative [Si]- α_{Si} relationship is not found in the model. The weak dependence of α_{Si} on [Si] may be explained by other factors discussed above that the model resolves, such as the balance of fluxes by fecal pellets versus aggregates or dust deposition. However, the absence of a clear relationship between [Si] and α_{Si} in the model pseudo-observations suggests both a strong role for the proposed frustule thickness mechanism in governing particulate organic carbon fluxes and a strong need for parameterizing it in ecosystem-biogeochemistry models.

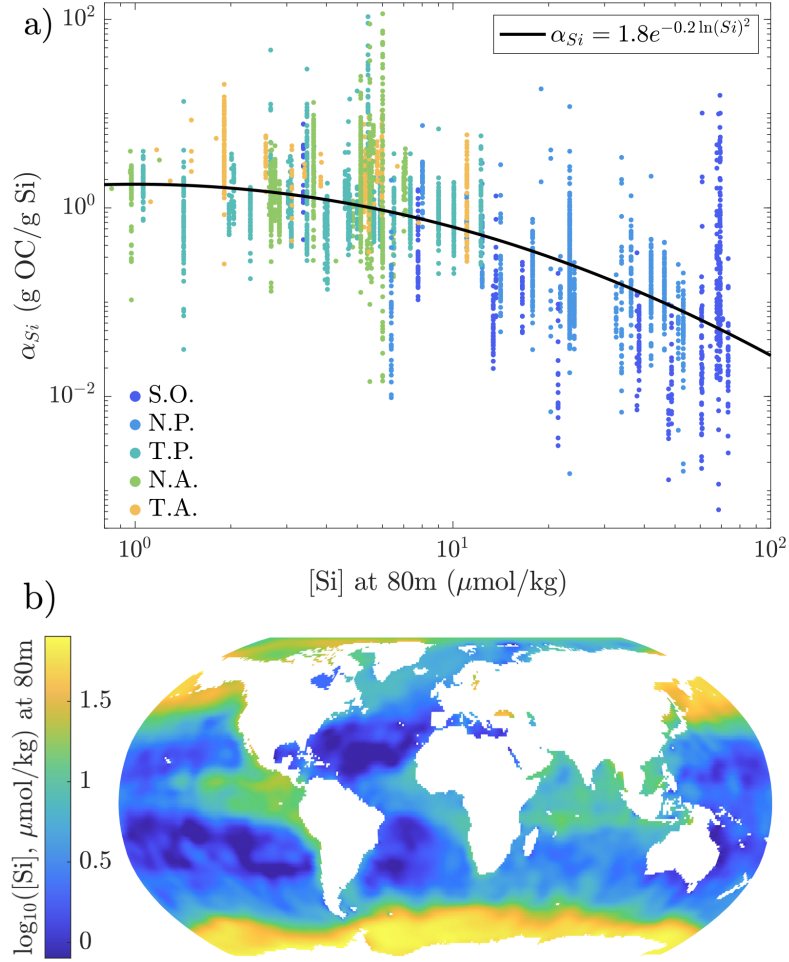


Figure 2. a) Silica ballasting coefficient as estimated by Equation 2 (Methods) versus silica concentration at 80m. Black line indicates empirical fit. b) Annual mean logarithmic silica concentration at 80m in the World Ocean Atlas.

3.5 Conclusion

Altogether these results suggest that the ballasting effect by opal varies a great deal in different parts of the ocean, and that much of this variation can be explained by local surface ocean silica concentrations. We argue that the most parsimonious explanation of this pattern is that it is due to diatom communities in silica-rich regions having more frustule mass per unit interior mass than those in silica-depleted regions. If diatom frustules protect the organic carbon inside them as they sink, such a silica concentration–opal ballasting relationship may occur irrespective of whether this is due to physiological plasticity or ecological selection, differences in diatom size or morphology, and whether the change in thickness is in response to metabolic constraints linked with availability of other nutrients or top-down effects linked to grazing pressure from zooplankton. The observed silica concentration–opal ballasting relationship could be parameterized in model diatoms; diatoms in silica-rich regions should have lower Si:C ratios (which could be captured e.g. with a quota scheme), and the remineralization of particulate organic carbon should decrease with particulate silica concentration more rapidly, than in silica-depleted regions. Other factors may also play a role, such as grazers’ preferences for thinner-frustuled diatoms (Assmy et al., 2013; Ryderheim et al., 2022), but could also in principle be parameterized. The very large gradients in silica concentration in the upper ocean (Figure 2b) suggest that the inclusion of this phenomenon could generate large changes for historical estimates and future projections of carbon export, particularly if this phenomenon substantially influences the distribution of Si (Matsumoto et al., 2002; Matsumoto & Sarmiento, 2008; Griffiths et al., 2013). Note however that the relationship in Figure 2a also includes a great deal of variability, which would have to be accounted for in such a parameterization e.g. by a transformation bias correction (Beauchamp & Olson, 1973). This variability is not surprising in light of the known variability in POC fluxes, with whose characteristics our model has been constructed to be consistent (Cael et al., 2018, 2021). Such a parameterization also constitutes a hypothesis which could be tested experimentally and further refined with measurements of diatoms’ stoichiometry, frustule thickness, and size, in different regions and/or across silica concentration gradients.

Acknowledgments

We thank Angelicque White, Thomas Kiørboe, and Ken Andersen for useful discussions. Cael, Henson and Jarníková acknowledge support by the National Environmental Research Council (NERC) Grant NE/T010622/1 CELOS (Constraining the Evolution of the southern Ocean carbon Sink), Le Quéré from the NERC Grant NE/V011103/1 Marine Frontiers, Guest from the Royal Society Grant RP.R1.191063, and Bowler from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (Diatomic; grant agreement No. 835067).

Open Research

The data used for this study are available from <https://doi.pangaea.de/10.1594/PANGAEA.855600> and <https://ncei.noaa.gov/access/world-ocean-atlas-2018/> and the code for their analysis is available for review purposes at <https://www.github.com/bbcael/opal> and will be deposited to a FAIR compliant repository if this article is eventually accepted. Model documentation and output are available at <https://www.uea.ac.uk/web/groups-and-centres/green-ocean/model>.

References

- Armand, L. K., Cornet-Barthaux, V., Mosseri, J., & Queguiner, B. (2008). Late summer diatom biomass and community structure on and around the naturally iron-fertilised kerguelen plateau in the southern ocean. *Deep Sea Research Part*

- 383 *II: Topical Studies in Oceanography*, 55(5-7), 653–676.
- 384 Armstrong, R. A., Lee, C., Hedges, J. I., Honjo, S., & Wakeham, S. G. (2001). A
385 new, mechanistic model for organic carbon fluxes in the ocean based on the
386 quantitative association of poc with ballast minerals. *Deep Sea Research Part*
387 *II: Topical Studies in Oceanography*, 49(1-3), 219–236.
- 388 Assmy, P., Smetacek, V., Montresor, M., Klaas, C., Henjes, J., Strass, V. H., ...
389 others (2013). Thick-shelled, grazer-protected diatoms decouple ocean carbon
390 and silicon cycles in the iron-limited antarctic circumpolar current. *Proceedings*
391 *of the National Academy of Sciences*, 110(51), 20633–20638.
- 392 Baker, C. A., Martin, A. P., Yool, A., & Popova, E. (2022). Biological carbon pump
393 sequestration efficiency in the north atlantic: a leaky or a long-term sink?
394 *Global Biogeochemical Cycles*, 36(6), e2021GB007286.
- 395 Barker, S., Higgins, J. A., & Elderfield, H. (2003). The future of the carbon cycle:
396 review, calcification response, ballast and feedback on atmospheric co₂. *Philos-*
397 *ophical Transactions of the Royal Society of London. Series A: Mathematical,*
398 *Physical and Engineering Sciences*, 361(1810), 1977–1999.
- 399 Beauchamp, J. J., & Olson, J. S. (1973). Corrections for bias in regression estimates
400 after logarithmic transformation. *Ecology*, 54(6), 1403–1407.
- 401 Bol, R., Henson, S. A., Rumyantseva, A., & Briggs, N. (2018). High-frequency
402 variability of small-particle carbon export flux in the northeast atlantic. *Global*
403 *Biogeochemical Cycles*, 32(12), 1803–1814.
- 404 Brzezinski, M. A., Olson, R. J., & Chisholm, S. W. (1990). Silicon availability and
405 cell-cycle progression in marine diatoms. *Marine ecology progress series*, 83–
406 96.
- 407 Buitenhuis, E. T., Le Quere, C., Bednaršek, N., & Schiebel, R. (2019). Large con-
408 tribution of pteropods to shallow caco₃ export. *Global Biogeochemical Cycles*,
409 33(3), 458–468.
- 410 Cael, B. (2021). Variability-based constraint on ocean primary production models.
411 *Limnology and Oceanography Letters*, 6(5), 262–269.
- 412 Cael, B., Bisson, K., Conte, M., Duret, M. T., Follett, C. L., Henson, S. A., ...
413 others (2021). Open ocean particle flux variability from surface to seafloor.
414 *Geophysical Research Letters*, 48(9), e2021GL092895.
- 415 Cael, B., Bisson, K., & Follett, C. L. (2018). Can rates of ocean primary production
416 and biological carbon export be related through their probability distributions?
417 *Global biogeochemical cycles*, 32(6), 954–970.
- 418 Campbell, J. W. (1995). The lognormal distribution as a model for bio-optical vari-
419 ability in the sea. *Journal of Geophysical Research: Oceans*, 100(C7), 13237–
420 13254.
- 421 Cram, J. A., Weber, T., Leung, S. W., McDonnell, A. M., Liang, J.-H., & Deutsch,
422 C. (2018). The role of particle size, ballast, temperature, and oxygen in the
423 sinking flux to the deep sea. *Global Biogeochemical Cycles*, 32(5), 858–876.
- 424 Ducklow, H. W., Steinberg, D. K., & Buesseler, K. O. (2001). Upper ocean carbon
425 export and the biological pump. *Oceanography*, 14(4), 50–58.
- 426 Efron, B., & Tibshirani, R. (1986). Bootstrap methods for standard errors, confi-
427 dence intervals, and other measures of statistical accuracy. *Statistical science*,
428 54–75.
- 429 Francois, R., Honjo, S., Krishfield, R., & Manganini, S. (2002). Factors controlling
430 the flux of organic carbon to the bathypelagic zone of the ocean. *Global Bio-*
431 *geochemical Cycles*, 16(4), 34–1.
- 432 Friedlingstein, P., O’Sullivan, M., Jones, M. W., Andrew, R. M., Gregor, L., Hauck,
433 J., ... others (2022). Global carbon budget 2022. *Earth System Science Data*,
434 14(11), 4811–4900.
- 435 Garcia, H., Weathers, K., Paver, C., Smolyar, I., Boyer, T., Locarnini, M., ... oth-
436 ers (2019). World ocean atlas 2018. vol. 4: Dissolved inorganic nutrients
437 (phosphate, nitrate and nitrate+ nitrite, silicate).

- Gnanadesikan, A. (1999). A global model of silicon cycling: Sensitivity to eddy parameterization and dissolution. *Global Biogeochemical Cycles*, 13(1), 199–220.
- Griffiths, J. D., Barker, S., Hendry, K. R., Thornalley, D. J., Van De Flierdt, T., Hall, I. R., & Anderson, R. F. (2013). Evidence of silicic acid leakage to the tropical atlantic via antarctic intermediate water during marine isotope stage 4. *Paleoceanography*, 28(2), 307–318.
- Heinze, C., Eyring, V., Friedlingstein, P., Jones, C., Balkanski, Y., Collins, W., ... others (2019). ESD reviews: Climate feedbacks in the earth system and prospects for their evaluation. *Earth System Dynamics*, 10(3), 379–452.
- Henson, S. A., Laufkötter, C., Leung, S., Giering, S. L., Palevsky, H. I., & Cavan, E. L. (2022). Uncertain response of ocean biological carbon export in a changing world. *Nature Geoscience*, 15(4), 248–254.
- Henson, S. A., Sanders, R., & Madsen, E. (2012). Global patterns in efficiency of particulate organic carbon export and transfer to the deep ocean. *Global Biogeochemical Cycles*, 26(1).
- Holzer, M., Primeau, F. W., DeVries, T., & Matear, R. (2014). The southern ocean silicon trap: Data-constrained estimates of regenerated silicic acid, trapping efficiencies, and global transport paths. *Journal of Geophysical Research: Oceans*, 119(1), 313–331.
- Klaas, C., & Archer, D. E. (2002). Association of sinking organic matter with various types of mineral ballast in the deep sea: Implications for the rain ratio. *Global biogeochemical cycles*, 16(4), 63–1.
- Kwon, E. Y., Primeau, F., & Sarmiento, J. L. (2009). The impact of remineralization depth on the air–sea carbon balance. *Nature Geoscience*, 2(9), 630–635.
- Le Quéré, C., Buitenhuis, E. T., Moriarty, R., Alvain, S., Aumont, O., Bopp, L., ... others (2016). Role of zooplankton dynamics for southern ocean phytoplankton biomass and global biogeochemical cycles. *Biogeosciences*, 13(14), 4111–4133.
- Malviya, S., Scalco, E., Audic, S., Vincent, F., Veluchamy, A., Poulain, J., ... others (2016). Insights into global diatom distribution and diversity in the world’s ocean. *Proceedings of the National Academy of Sciences*, 113(11), E1516–E1525.
- Marsay, C. M., Sanders, R. J., Henson, S. A., Pabortsava, K., Achterberg, E. P., & Lampitt, R. S. (2015). Attenuation of sinking particulate organic carbon flux through the mesopelagic ocean. *Proceedings of the National Academy of Sciences*, 112(4), 1089–1094.
- Martin, J. H., Knauer, G. A., Karl, D. M., & Broenkow, W. W. (1987). Vertex: carbon cycling in the northeast pacific. *Deep Sea Research Part A. Oceanographic Research Papers*, 34(2), 267–285.
- Martin-Jézéquel, V., Hildebrand, M., & Brzezinski, M. A. (2000). Silicon metabolism in diatoms: implications for growth. *Journal of phycology*, 36(5), 821–840.
- Matsumoto, K., & Sarmiento, J. L. (2008). A corollary to the silicic acid leakage hypothesis. *Paleoceanography*, 23(2).
- Matsumoto, K., Sarmiento, J. L., & Brzezinski, M. A. (2002). Silicic acid leakage from the southern ocean: A possible explanation for glacial atmospheric pco₂. *Global Biogeochemical Cycles*, 16(3), 5–1.
- Mouw, C. B., Barnett, A., McKinley, G. A., Gloege, L., & Pilcher, D. (2016). Global ocean particulate organic carbon flux merged with satellite parameters. *Earth System Science Data*, 8(2), 531–541.
- Pančić, M., Torres, R. R., Almeda, R., & Kjørboe, T. (2019). Silicified cell walls as a defensive trait in diatoms. *Proceedings of the Royal Society B*, 286(1901), 20190184.
- Parekh, P., Follows, M. J., Dutkiewicz, S., & Ito, T. (2006). Physical and biological regulation of the soft tissue carbon pump. *Paleoceanography*, 21(3).
- Petrou, K., Baker, K. G., Nielsen, D. A., Hancock, A. M., Schulz, K. G., & David-

- son, A. T. (2019). Acidification diminishes diatom silica production in the southern ocean. *Nature Climate Change*, 9(10), 781–786.
- Pondaven, P., Gallinari, M., Chollet, S., Bucciarelli, E., Sarthou, G., Schultes, S., & Jean, F. (2007). Grazing-induced changes in cell wall silicification in a marine diatom. *Protist*, 158(1), 21–28.
- Qiu, B., & Huang, R. X. (1995). Ventilation of the north atlantic and north pacific: subduction versus obduction. *Journal of Physical Oceanography*, 25(10), 2374–2390.
- Round, F. E., Crawford, R. M., & Mann, D. G. (1990). *Diatoms: biology and morphology of the genera*. Cambridge university press.
- Ryderheim, F., Grønning, J., & Kiørboe, T. (2022). Thicker shells reduce copepod grazing on diatoms. *Limnology and Oceanography Letters*.
- Sarmiento, J. L., Gruber, N., Brzezinski, M., & Dunne, J. (2004). High-latitude controls of thermocline nutrients and low latitude biological productivity. *Nature*, 427(6969), 56–60.
- Sarmiento, J. L., Simeon, J., Gnanadesikan, A., Gruber, N., Key, R., & Schlitzer, R. (2007). Deep ocean biogeochemistry of silicic acid and nitrate. *Global Biogeochemical Cycles*, 21(1).
- Siegel, D., DeVries, T., Doney, S., & Bell, T. (2021). Assessing the sequestration time scales of some ocean-based carbon dioxide reduction strategies. *Environmental Research Letters*, 16(10), 104003.
- Tréguer, P., Bowler, C., Moriceau, B., Dutkiewicz, S., Gehlen, M., Aumont, O., ... others (2018). Influence of diatom diversity on the ocean biological carbon pump. *Nature Geoscience*, 11(1), 27–37.
- Wilson, J. D., Barker, S., & Ridgwell, A. (2012). Assessment of the spatial variability in particulate organic matter and mineral sinking fluxes in the ocean interior: Implications for the ballast hypothesis. *Global Biogeochemical Cycles*, 26(4).
- Wright, R. M., Le Quéré, C., Buitenhuis, E., Pitois, S., & Gibbons, M. J. (2021). Role of jellyfish in the plankton ecosystem revealed using a global ocean biogeochemical model. *Biogeosciences*, 18(4), 1291–1320.

A global ocean opal ballasting–silica relationship

B. B. Cael¹, C. Mark Moore², Joe Guest³, Tereza Jarníková³, Colleen B. Mouw⁴, Chris Bowler^{5,6}, Edward Mawji¹, Stephanie A. Henson¹, and Corinne Le Quéré³

¹National Oceanography Centre, Southampton, UK

²School of Ocean and Earth Science, University of Southampton, UK

³School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, UK

⁴University of Rhode Island, Graduate School of Oceanography, Narragansett, RI, USA

⁵Institut de Biologie de l'Ecole Normale Supérieure (IBENS), Ecole Normale Supérieure, CNRS,

INSERM, Université PSL, 75005 Paris, France

⁶Stazione Zoologica Anton Dohrn, Naples, Italy

Key Points:

- Opal ballasting (particulate organic carbon flux per opal flux) varies 6-fold across ocean regions; calcium carbonate ballasting is uniform.
- Silica concentration predicts opal ballasting which suggests that the latter occurs via mineral protection and varies with diatom frustule thickness.
- This ballasting pattern's absence from a sophisticated biogeochemical model indicates the need for a novel mechanistic parameterization.

Corresponding author: B. B. Cael, cael@noc.ac.uk

Abstract

Opal and calcium carbonate are thought to regulate the biological pump's transfer of organic carbon to the deep ocean. A global sediment trap database exhibits large regional variations in the organic carbon flux associated with opal flux. These variations are well-explained by upper ocean silica concentrations, with high opal 'ballasting' in the silica-deplete tropical Atlantic Ocean, and low ballasting in the silica-rich Southern Ocean. A plausible, testable hypothesis is that opal ballasting is due to mineral protection, and varies because diatoms grow thicker frustules where silica concentrations are higher, protecting less organic carbon per unit opal. These patterns do not emerge in an advanced ocean biogeochemical model when opal ballasting is represented using a single global parameterization for diatoms, indicating the need for additional parameterization of the dependence of diatoms traits on silica concentration to capture the links between elemental cycles and future changes in the biological pump.

Plain Language Summary

Opal, or hydrated silica, is taken up in the surface ocean by diatoms, which use it to construct their protective frustules. Another type of plankton, coccolithophores, generate protective platelets from calcium carbonate. These two minerals, and thereby plankton types, play major roles in the cycling of carbon globally. The 'biological carbon pump' transfers carbon from the atmosphere to the ocean's depths, where it can stay for centuries to millennia. This process has influenced past atmospheric carbon dioxide concentrations and could also influence future carbon dioxide concentrations and hence climate. The transfer of carbon to the deep ocean is known to be partially regulated by the amount of 'ballast' minerals in sinking particles, especially opal and calcium carbonate, which are denser and cause particles to sink faster and/or protect organic carbon from microbial consumption. Here we show that unlike calcium carbonate, the ballasting effect of opal varies a great deal between different regions of the ocean. The variation in opal ballasting is well-explained by the upper-ocean concentration of silica in these regions. This suggests a simple explanation: when silica concentrations are high/low, diatoms grow thick/thin frustules. Including this process in carbon cycle models may improve their ability to predict future biogeochemical cycles and climate.

1 Introduction

The biological carbon pump (BCP) entails the uptake, processing and transfer of organic carbon to the deep ocean by biological processes. Without the BCP, atmospheric CO₂ levels would be ~200 ppm higher than they currently are (Parekh et al., 2006; Kwon et al., 2009). Particulate organic carbon (POC) and associated nutrients sinking out of the ocean's upper layer are gradually remineralized by grazing processes and microbial activity. The depth at which POC is remineralized determines the water mass that the resulting inorganic carbon enters, and thus the timescales of potential re-exchange with the atmosphere. Generally, the deeper POC can penetrate into the ocean, the longer it is stored (Siegel et al., 2021; Baker et al., 2022). However, the mechanistic processes that underlie the considerable spatial and temporal variability in POC flux and remineralization (Cram et al., 2018; Bol et al., 2018) are still debated (Henson et al., 2022). One hypothesis posits that a portion of sinking POC is associated with 'ballast minerals', i.e. calcium carbonate and biogenic silica generated by calcifying organisms and diatoms, respectively (Armstrong et al., 2001; Klaas & Archer, 2002). These are thought to deepen the remineralization depth of POC either through protection of the POC, or by increasing the particles' excess density and thus sinking speed. Although the presence of ballast minerals has a strong statistical relationship with remineralization depth, a lack of mechanistic understanding introduces challenges for parameterising ballasting in Earth

system models, despite its potential to be an important component of carbon cycle-climate feedbacks (Barker et al., 2003; Petrou et al., 2019; Heinze et al., 2019).

Our objectives here are to diagnose i) the ballast effects of opal and calcium carbonate (in terms of the POC flux at a reference depth associated with a unit of opal or calcium carbonate flux), ii) the extent to which the ballasting effects vary among ocean regions, iii) the drivers of regional variations, and iv) the need to introduce new parameterizations in global ocean biogeochemical models. To achieve these objectives, we apply a statistical model based on the robust log-normality of ocean particle fluxes (Cael et al., 2018, 2021) to a global sediment trap database (Mouw et al., 2016). We find that, while the majority of parameters of the statistical model remain fairly constant, the ballasting by opal varies by almost an order of magnitude between different large regions. We discuss various possible mechanisms to explain this regional difference but identify one that is most parsimonious and plausible based on upper ocean silica availability and diatom frustule thickness, which constitutes a hypothesis that is experimentally testable. We show that this relationship does not occur in a state-of-the-art ocean biogeochemical model (Buitenhuis et al., 2019), underscoring that the opal ballasting pattern that we uncover here is produced by a currently unparameterized process. We then develop an easily implementable parameterization for opal ballasting based on silica concentration.

2 Methods

2.1 Statistical Model

Following (Cael et al., 2018, 2021), our statistical model is derived from treatment of particle flux variability as log-normal. This is based on the empirically validated (Cael et al., 2018, 2021; Cael, 2021) argument that i) net primary production varies log-normally because multiple conditions need to be met in order for production to occur, such that the ‘law of necessary conditions’ applies, ii) particle export out of the euphotic layer is equal to net primary production times export efficiency by definition, and export efficiency is a variable quantity, and iii) particle flux at a given depth is equal to particle export times the transfer efficiency to that depth, which is also a variable quantity. If the fluxes of particulate organic carbon ($\mathcal{F}_{OC}$ ($\text{mg C m}^{-2} \text{ d}^{-1}$), particulate inorganic carbon ($\mathcal{F}_{IC}$ ($\text{mg C m}^{-2} \text{ d}^{-1}$, i.e. calcium carbonate in units of C mass), and particulate silica ($\mathcal{F}_{Si}$ ($\text{mg S m}^{-2} \text{ d}^{-1}$, i.e. opal in units of S mass), are log-normally distributed (Cael et al., 2021), and the latter both act in concert as ballasting minerals (i.e. organic carbon flux to a given depth can be facilitated by either or both minerals and does not necessarily require both), then they should be related by an equation of the form (Campbell, 1995)

$$\mathcal{F}_{OC} = (\alpha_{IC}\mathcal{F}_{IC} + \alpha_{Si}\mathcal{F}_{Si})^\gamma z^{\Delta b} \quad (1)$$

where α_{IC} (dimensionless) is the flux of organic carbon associated with a unit of inorganic carbon, α_{Si} (g C/g Si) is the flux of organic carbon associated with a unit of silica, γ (dimensionless) is the degree of sub-/super-linearity in the scaling relationship between organic carbon fluxes and ballast mineral fluxes, and Δb is the difference in the vertical attenuation (using a power-law approximation (Martin et al., 1987)) of organic carbon flux versus ballast mineral flux. Here z is normalized to a given reference depth z_o , for which we use 1km. Our results are not affected by this choice. Hence Δb encodes the extent to which organic carbon flux attenuates with depth to z_o , i.e. 1km, compared to ballast mineral flux. γ can be interpreted as the extent to which the effect of ballast minerals have ‘diminishing returns’ because if $\gamma < 1$ and increasingly so as $\gamma \rightarrow 0$, particles with e.g. twice the ballast mineral loading will have less than twice the organic carbon content (γ can in principle be > 1 but this is mechanistically implausible and is not

seen in the observations). α_{IC} and α_{Si} can be interpreted as the organic carbon flux per unit of each ballast mineral flux at the reference depth; strictly speaking this is only true when $\gamma = 1$, but regardless of the value of γ the ratio of the α values captures the relative ballast effect per unit mass of each mineral. (Note that Equation 1 is equivalent to the one given in (Cael et al., 2021), with Δb used here in replacement of b to make it explicit that this parameter captures the *difference* in vertical attenuation of organic carbon versus ballast mineral fluxes, $\alpha_{IC} = \kappa^{1/\gamma}$ and $\alpha_{Si} = \beta\kappa^{1/\gamma}$ used in replacement of κ and β to make the ballast effect of each mineral explicit parameters, and a reference depth of 1km used rather than 3500m because measurements of the full water column are considered rather than just near-bottom sediment traps.)

2.2 Sediment Trap Data

We utilized a global dataset of POC, PIC, and particulate silica (PSi) flux estimated from POC, PIC, and PSi concentration observations from sediment traps (Mouw et al., 2016). The database also includes ^{234}Th -based POC fluxes and the fluxes of other elements and molecules, but we only analyze coincident POC, PIC, and PSi flux measurements from sediment traps. Data were compiled from public repositories and directly from the literature. When CaCO_3 fluxes were reported and PIC fluxes were not, the former were converted to the latter using the ratio of their molar masses; the same was done for SiO_2 and Si(OH)_4 to PSi fluxes. The data set contains 15,792 individual POC flux estimates, measured on timescales of days to weeks, at 674 unique locations collected between 1976 and 2012. 85% of the observations are concentrated in the Northern Hemisphere. Most of the dataset (71%) was measured at $\geq 500\text{m}$, with the most common deployment depths between 1000–1500 m.

These data are split into five broad geographic regions. The Southern Ocean (SO) is defined here as all data poleward of 30°S ; the North Pacific (NP) and Atlantic (NA) are defined as all data poleward of 30°N in each basin; the Tropical Pacific (TP) and Atlantic (TA) are defined as all data equatorward of 30° in each basin. (There are few measurements in the Indian Ocean.) The data from major time-series sites were excluded from our analyses, as the database is unavoidably very spatially biased even without including these sites, and these locations would be vastly over-represented if included, such that our global analysis would be largely dictated by the behavior of a few locations (the majority with low silica concentrations, furthermore). Excluding these locations, the database includes 768/2274/2286/1327/504 co-located measurements of $\mathcal{F}_{OC}$, $\mathcal{F}_{IC}$, and $\mathcal{F}_{Si}$ in the SO/NP/TP/NA/TA respectively.

2.3 Statistical Analysis

Equation 1 is then fit to the data from each region following the procedure in (Cael et al., 2021). The $(\alpha_{Si}/\alpha_{IC}, \Delta b)$ that yields the best fit regression, using a scaling relationship of the form $y \propto x^\gamma$, between $\mathcal{F}_{OC}z^{\Delta b}$ and $\mathcal{F}_{IC} + \frac{\alpha_{Si}}{\alpha_{IC}}\mathcal{F}_{Si}$ is identified. Major axis type II regression is used to account for the fact that uncertainties exist on both the x - and y -axis. Multiplicative (i.e., % rather than absolute) errors are assumed, consistent with these variables scaling with one another and being log-normally distributed. Parameter uncertainties are calculated via bootstrap resampling (Efron & Tibshirani, 1986) with 1,000 bootstrap reiterations.

Equation 1 can be inverted to estimate the opal ballasting α_{Si} for each individual measurement. This can be done by taking the measured fluxes of OC, IC, and Si and the measurement depth, along with a representative global value for γ , Δb , and α_{IC} (here we use the mean across regions as these other parameters are fairly constant between regions, see §3), and rearranging Equation 1 to yield

$$\alpha_{Si} = \frac{1}{\mathcal{F}_{Si}} \left((\mathcal{F}_{OC} z^{-\Delta b})^{1/\gamma} - \alpha_{IC} \mathcal{F}_{IC} \right) \quad (2)$$

This estimate of α_{Si} is then compared to co-located upper ocean silica concentrations ($[\text{Si}]$, ($\mu\text{mol/kg}$)) to test the hypothesis that higher $[\text{Si}]$ values are associated with lower α_{Si} values. $[\text{Si}]$ values were taken from the World Ocean Atlas 2018 (Garcia et al., 2019). The 80m depth at which $[\text{Si}]$ is considered here was selected as the depth at which the Spearman rank correlation between $[\text{Si}]$ at that depth and the inferred α_{Si} at the same latitude and longitude is a maximum. For 80m, the correlation is 0.68. Our results are not sensitive to this choice; the correlation for all depths 0-500m is ≥ 0.65 . The logarithm of α_{Si} is then regressed against the logarithm of $[\text{Si}]$ (at 80m) using the second-order polynomial of the form $y = p_2 x^2 + p_0$, to capture heuristically that α_{Si} asymptotes to a constant value as $[\text{Si}] \rightarrow 0$. Adding the term $p_1 x$ yielded no difference as the p_1 term was not significantly different from zero.

2.4 Numerical Model

A global ocean biogeochemical model is used to explore if the properties inferred using the database emerge in the current generation of models. We use the NEMO-PlankTOM12 model which represents explicitly twelve Plankton Functional Types (PFTs), six phytoplankton types (picophytoplankton, N_2 -fixers, diatoms, *Phaeocystis*, and other mixed-phytoplankton), five zooplankton (protozooplankton, mesozooplankton, crustacean and gelatinous macrozooplankton, and pteropods) and bacteria (Buitenhuis et al., 2019; Le Quéré et al., 2016; Wright et al., 2021). All PFTs are represented using vital parameters of growth and loss rates based on available observations, and interact with each other using food preferences generally based on size. Growth rates are based on temperature and vary with nutrient availability. The model includes a full silicate cycle, with its dissolved, biogenic (with a fixed Si:C ratio for diatoms) and detrital pools. Sinking of organic matter is a function of the ballasting density of the particles. Full equations are presented in the supplementary of (Le Quéré et al., 2016), with additional parameterization of calcium carbonate as in (Buitenhuis et al., 2019). The model is embedded in the NEMOv3.6 general ocean circulation model, and is forced with NCEP reanalysis data. Compared to its last published version described in (Friedlingstein et al., 2022), the model introduces a simple sediment model which stores material from sinking fluxes in an additional bottom layer. To maintain mass balance, nutrients are removed from the sediment layer to equalize the river and dust fluxes. The model also includes further optimization of global parameters to reproduce the size and vertical profiles of the observed organic carbon, silica and calcium carbonate sinking rates presented here.

3 Results & Discussion

3.1 Regional Scaling Relationships

Figure 1 shows the fit of Equation 1 to the sediment trap data in each region. In each case, $\mathcal{F}_{OC}$ is well-predicted from ballast fluxes, with $r^2 = 0.70 - 0.81$. The parameters α_{IC} , γ , and Δb vary little between regions, with coefficients of variation of 10%, 6%, and 24% respectively (these parameters are discussed below). By contrast, the ballast effect of opal, α_{Si} , has a coefficient of variation of 77%, and varies by more than 6-fold between regions from a value of 1.3 ± 0.2 g C/g Si in the Tropical Atlantic to a value of 0.20 ± 0.02 g C/g Si in the Southern Ocean. In other words, in the Tropical Atlantic 1 mg Si $\text{m}^{-2} \text{d}^{-1}$ of opal flux is associated with more than six times more organic carbon flux at 1km than 1 mg Si $\text{m}^{-2} \text{d}^{-1}$ of opal flux in the Southern Ocean. The highest α_{Si} values are found in the Atlantic, then the Pacific and then the Southern Ocean, and within the Atlantic and Pacific Oceans, the tropical regions have larger α_{Si} values than the Northern regions (Figure 1f). Altogether there appears to be a very large dif-

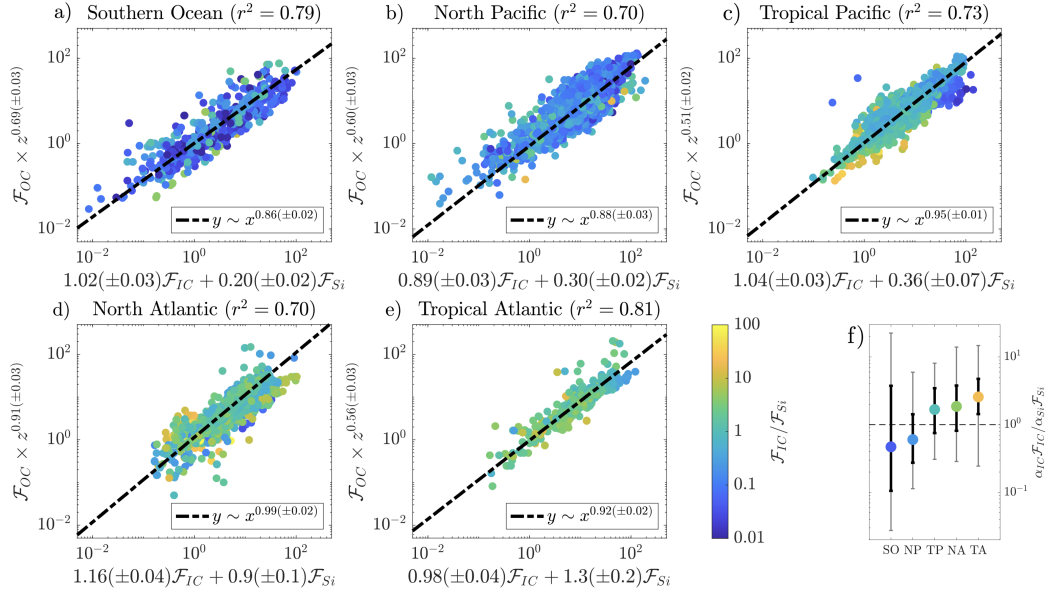


Figure 1. a-e) Scaling relationships corresponding to Equation 1 between organic carbon and ballast fluxes for different large regions. Color indicates ratio of fluxes of different ballast minerals. Parameter estimates are given on x- and y-axis labels. Units on both axes are $\text{mg C m}^{-2} \text{d}^{-1}$. Parameter values and uncertainties are estimated as described in the Methods. f) Median, interquartile range, and 95% range of ratio of POC flux at 1km estimated to be associated with inorganic carbon vs. opal (i.e. $\alpha_{IC}\mathcal{F}_{IC}/\alpha_{Si}\mathcal{F}_{Si}$) for each region. Dashed black line corresponds to equal organic carbon flux associated with each ballast mineral.

ference in the Si associated mineral ballasting between different ocean regions, with potentially large implications for ocean biogeochemical cycling.

Despite the much smaller α_{Si} values in the Southern Ocean and North Pacific, the far larger $\mathcal{F}_{Si}$ fluxes in these regions also mean that opal is associated with more POC flux at 1km than inorganic carbon for a majority of measurements in those regions (Figure 1f), captured by the ratio $\alpha_{IC}\mathcal{F}_{IC}/\alpha_{Si}\mathcal{F}_{Si}$. In the other three regions, calcium carbonate is associated with more POC flux at 1km, i.e. $\alpha_{IC}\mathcal{F}_{IC} > \alpha_{Si}\mathcal{F}_{Si}$, for a majority of measurements, as has often been reported in the literature (Klaas & Archer, 2002; Francois et al., 2002; Armstrong et al., 2001; Wilson et al., 2012). The large variability of this ratio between measurements in all regions, however, underscores that both ballast minerals play important roles; the interquartile range of $\alpha_{IC}\mathcal{F}_{IC}/\alpha_{Si}\mathcal{F}_{Si}$ spans values from <1 to >1 for all regions besides the tropical Pacific. (Note that this ratio is insensitive to whether molar or mass units are used.)

Parameters other than α_{Si} are fairly uniform across regions and change in plausible ways in light of the processes controlling the biological pump. α_{IC} is nearly constant between regions, consistent with PIC either increasing particles' excess density or protecting POC similarly between regions. γ is slightly <1 in all regions except the North Atlantic, but only slightly so, indicating some degree of 'diminishing returns' on the effect of ballast minerals, but not enough to make as large a difference to POC fluxes as variations in α_{Si} . Δb is higher at higher latitudes, consistent with some sediment-trap derived patterns for b (Henson et al., 2012), though other studies find the opposite pattern (Marsay et al., 2015). Note that we do not find systematic behavior with depth in the residuals, which suggests that a power-law approximation of flux attenuation with

depth is suitable for our analysis. We do not consider the variations in these parameters further.

3.2 Possible Mechanisms

A simple and arguably parsimonious explanation for the regional variations in α_{Si} is that variations in α_{Si} are determined by upper ocean silica concentrations ($[Si]$, $\mu\text{mol/kg}$). Indeed, $[Si]$ is lowest in the surface waters of the Atlantic and highest in the Southern Ocean, due to the interaction of the meridional overturning circulation with both the temperature dependent long remineralization length scale of Si and high Si:N uptake ratios in the surface Southern Ocean (Sarmiento et al., 2007, 2004; Holzer et al., 2014; Gnanadesikan, 1999). Globally Si is largely trapped in the Southern Ocean (Holzer et al., 2014) where ventilation of Si-rich deep waters is coupled to high production and export of P_{Si} which is largely remineralized at depths below the northward flowing Antarctic intermediate and sub-Antarctic mode waters (AAIW/SAMW) (Sarmiento et al., 2007). Outside the Southern Ocean, the Atlantic is filled by the upper branch of the overturning circulation, which is ventilated by AAIW/SAMW formed within the relatively Si-depleted lower latitudes of the Southern Ocean (Sarmiento et al., 2004), while the Pacific is filled more by the lower branch, which is ventilated by the relatively Si-rich higher latitudes in the Southern Ocean. Furthermore, tropical regions in the Atlantic and Pacific are more Si-depleted than their Northern counterparts because some ventilation of deep waters occurs at high latitudes, even in the Pacific (Qiu & Huang, 1995). As a result, Atlantic diatoms grow in the most Si-depleted conditions and Southern Ocean diatoms grow in the most Si-replete conditions, with tropical diatoms growing in intermediate Si concentrations. The more Si-deplete the conditions in which diatoms grow, the less opportunity diatoms have to meet or exceed their minimum quota of silica. This will tend to lead to lower Si:C stoichiometry for diatoms in more Si-deplete conditions, meaning thinner-frustuled diatoms of a given size and/or larger diatoms (because silica is predominantly contained in diatoms' frustules, whereas carbon is predominantly contained in diatoms' interiors). If opal ballasting is due to protection of organic carbon by intact diatom frustules rather than a particle-density-driven effect, then thinner or larger frustules will correspond to more protection of organic carbon per unit opal, and hence larger α_{Si} . (In general, large variations in α_{Si} between regions are consistent with a mineral protection mechanism rather than a particle density mechanism for ballasting; opal's chemical characteristics do not vary by region, so the extent to which its inclusion in particles affects their density and thereby sinking speed should not be expected to vary regionally.) Diatoms in the Southern Ocean, and to a lesser extent in the (North) Subarctic Pacific, will thus be expected to have more ability to make thicker frustules in order to protect themselves from grazers, as observed (Assmy et al., 2013; Pančić et al., 2019), which results in higher Si:C ratios and lower α_{Si} values. We thus hypothesize that there should be a negative relationship between α_{Si} and $[Si]$ (see §3.3).

Several other factors may complicate this simple explanation for regional variation in α_{Si} . Different diatom taxa are characterized by different morphologies with widely varying sizes and silica frustule pattern variations (Round et al., 1990). Different diatom species also exhibit specific biogeographies, inhabiting different ocean regions (Tréguer et al., 2018; Malviya et al., 2016). Sporulation of diatoms, especially of those abundant in the Southern Ocean such as *Chaetoceros*, may also influence the Si:C of organic material sinking into the deep sea (Armand et al., 2008). The different compositions of diatom communities in different oceanic regions will therefore impact opal ballasting, but may in turn be influenced by the global availability of Si (Figure 2b). Furthermore, the Si content of diatom frustules can be impacted by environmental conditions other than $[Si]$. Silicification of diatoms is tightly linked to the cell cycle of growth, with Si uptake primarily occurring during the G2 interphase (Martin-Jézéquel et al., 2000). If the availability of other nutrients needed for cell growth (nitrate, phosphate, or iron) or other external growth conditions slow or prolong the G2 phase of the cell cycle in diatoms, sili-

cification and diatom ballast increases. It has also been reported that increased grazing pressure may also lead to more heavily silicified diatoms (Pondaven et al., 2007) presumably as a mechanism for organisms to enhance their protection from grazing losses. In contrast, Si deficiency is the only condition that acts to reliably lower the silica content of the diatom cell wall (Brzezinski et al., 1990). All these factors are likely to impact the formation and degradation of particles. Fecal pellets can also contribute appreciably to POC fluxes and their stoichiometry is necessarily reflective of their prey (Ducklow et al., 2001), so the selective grazing of diatoms of different frustule thicknesses (Ryderheim et al., 2022) and the relative balance of fecal pellets and aggregates in total POC fluxes will also play a role. Additionally, dust deposition is known to vary between regions and may further affect particles directly by being incorporated as lithogenic ballast (n.b. these are not collated in the (Mouw et al., 2016) database) or indirectly by supplying nutrients such as iron and thereby influencing phytoplankton communities.

3.3 Silica–Opal Ballasting Relationship

To test for a relationship between α_{Si} and [Si] more quantitatively, we use Equation 2 to estimate α_{Si} for each sediment trap measurement. For (α_{IC} , Δb and γ) we use the means over the five regions (= 1.02, 0.65, 0.92 respectively). Our results are not sensitive to these parameter values. We then compare these estimates to the co-located [Si] (at 80m depth). Figure 2a shows that the estimated α_{Si} decreased from a value of ~ 1.8 when [Si] $\rightarrow 0$, to small values as [Si] becomes large. This relationship is approximately described by the function $\alpha_{Si} = 1.8e^{-0.2\ln[Si]^2}$ ($r^2 = 0.49$, $p \ll 0.01$). Decreasing α_{Si} with increasing [Si] is consistent with the hypothesis presented above, as low-[Si] regions would correspond to thinner diatom frustules and more protected organic carbon per unit [Si], and the opposite for high-[Si] regions.

3.4 Model Simulation

To test for whether the observed [Si]- α_{Si} relationship is found in a numerical model’s historical simulation that does not parameterize the proposed frustule thickness mechanism, we sample the model analogously to how the real ocean has been sampled and repeat the same analysis on the pseudo-observations. Specifically, we draw $\mathcal{F}_{OC/IC/Si}$ values at the same latitudes, longitudes, depths, and months for which we have sediment trap measurements from monthly model output, using a randomly selected model year, 2000. Neither sub-monthly nor interannual variations should affect the relationship we investigate here. We also draw corresponding [Si] values at 80m depth. We then repeat the analysis from §2.3 on these data. We use the observational regional means of (α_{IC} , Δb and γ) as in §3.3. Our results are not affected by using the regional means for model pseudo-observations or using parameter combinations from specific observed or modeled regions.

We find a negative but far weaker relationship between model [Si] and inferred α_{Si} , with a correlation coefficient of -0.18 (compared to -0.67 for the observations). For a relationship of the form $y = p_2x^2 + p_0$ as fit to the observations above, the r^2 is 0.05 with $p_2 = +0.067 \pm 0.004$, compared to $r^2 = 0.49$ with $p_2 = -0.202 \pm 0.003$ for the observations. Thus the observed strong negative [Si]- α_{Si} relationship is not found in the model. The weak dependence of α_{Si} on [Si] may be explained by other factors discussed above that the model resolves, such as the balance of fluxes by fecal pellets versus aggregates or dust deposition. However, the absence of a clear relationship between [Si] and α_{Si} in the model pseudo-observations suggests both a strong role for the proposed frustule thickness mechanism in governing particulate organic carbon fluxes and a strong need for parameterizing it in ecosystem-biogeochemistry models.

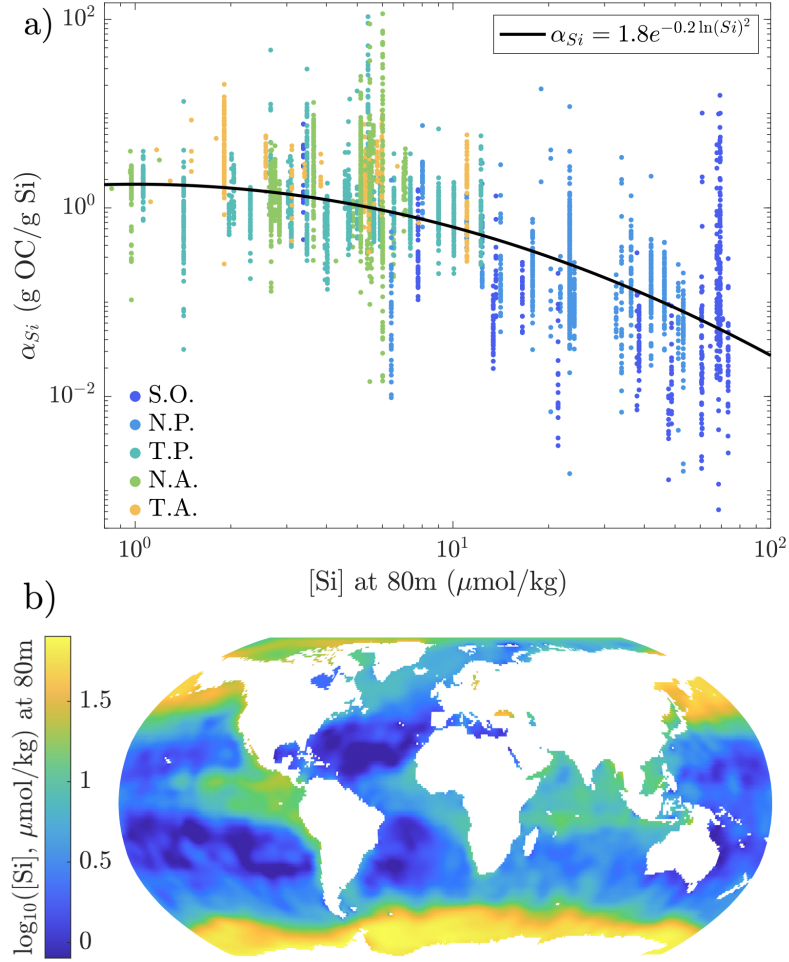


Figure 2. a) Silica ballasting coefficient as estimated by Equation 2 (Methods) versus silica concentration at 80m. Black line indicates empirical fit. b) Annual mean logarithmic silica concentration at 80m in the World Ocean Atlas.

3.5 Conclusion

Altogether these results suggest that the ballasting effect by opal varies a great deal in different parts of the ocean, and that much of this variation can be explained by local surface ocean silica concentrations. We argue that the most parsimonious explanation of this pattern is that it is due to diatom communities in silica-rich regions having more frustule mass per unit interior mass than those in silica-depleted regions. If diatom frustules protect the organic carbon inside them as they sink, such a silica concentration–opal ballasting relationship may occur irrespective of whether this is due to physiological plasticity or ecological selection, differences in diatom size or morphology, and whether the change in thickness is in response to metabolic constraints linked with availability of other nutrients or top-down effects linked to grazing pressure from zooplankton. The observed silica concentration–opal ballasting relationship could be parameterized in model diatoms; diatoms in silica-rich regions should have lower Si:C ratios (which could be captured e.g. with a quota scheme), and the remineralization of particulate organic carbon should decrease with particulate silica concentration more rapidly, than in silica-depleted regions. Other factors may also play a role, such as grazers’ preferences for thinner-frustuled diatoms (Assmy et al., 2013; Ryderheim et al., 2022), but could also in principle be parameterized. The very large gradients in silica concentration in the upper ocean (Figure 2b) suggest that the inclusion of this phenomenon could generate large changes for historical estimates and future projections of carbon export, particularly if this phenomenon substantially influences the distribution of Si (Matsumoto et al., 2002; Matsumoto & Sarmiento, 2008; Griffiths et al., 2013). Note however that the relationship in Figure 2a also includes a great deal of variability, which would have to be accounted for in such a parameterization e.g. by a transformation bias correction (Beauchamp & Olson, 1973). This variability is not surprising in light of the known variability in POC fluxes, with whose characteristics our model has been constructed to be consistent (Cael et al., 2018, 2021). Such a parameterization also constitutes a hypothesis which could be tested experimentally and further refined with measurements of diatoms’ stoichiometry, frustule thickness, and size, in different regions and/or across silica concentration gradients.

Acknowledgments

We thank Angelicque White, Thomas Kiørboe, and Ken Andersen for useful discussions. Cael, Henson and Jarníková acknowledge support by the National Environmental Research Council (NERC) Grant NE/T010622/1 CELOS (Constraining the Evolution of the southern Ocean carbon Sink), Le Quéré from the NERC Grant NE/V011103/1 Marine Frontiers, Guest from the Royal Society Grant RP.R1.191063, and Bowler from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (Diatomic; grant agreement No. 835067).

Open Research

The data used for this study are available from <https://doi.pangaea.de/10.1594/PANGAEA.855600> and <https://ncei.noaa.gov/access/world-ocean-atlas-2018/> and the code for their analysis is available for review purposes at <https://www.github.com/bbcael/opal> and will be deposited to a FAIR compliant repository if this article is eventually accepted. Model documentation and output are available at <https://www.uea.ac.uk/web/groups-and-centres/green-ocean/model>.

References

- Armand, L. K., Cornet-Barthaux, V., Mosseri, J., & Queguiner, B. (2008). Late summer diatom biomass and community structure on and around the naturally iron-fertilised kerguelen plateau in the southern ocean. *Deep Sea Research Part*

- 383 *II: Topical Studies in Oceanography*, 55(5-7), 653–676.
- 384 Armstrong, R. A., Lee, C., Hedges, J. I., Honjo, S., & Wakeham, S. G. (2001). A
385 new, mechanistic model for organic carbon fluxes in the ocean based on the
386 quantitative association of poc with ballast minerals. *Deep Sea Research Part*
387 *II: Topical Studies in Oceanography*, 49(1-3), 219–236.
- 388 Assmy, P., Smetacek, V., Montresor, M., Klaas, C., Henjes, J., Strass, V. H., ...
389 others (2013). Thick-shelled, grazer-protected diatoms decouple ocean carbon
390 and silicon cycles in the iron-limited antarctic circumpolar current. *Proceedings*
391 *of the National Academy of Sciences*, 110(51), 20633–20638.
- 392 Baker, C. A., Martin, A. P., Yool, A., & Popova, E. (2022). Biological carbon pump
393 sequestration efficiency in the north atlantic: a leaky or a long-term sink?
394 *Global Biogeochemical Cycles*, 36(6), e2021GB007286.
- 395 Barker, S., Higgins, J. A., & Elderfield, H. (2003). The future of the carbon cycle:
396 review, calcification response, ballast and feedback on atmospheric co₂. *Philos-*
397 *ophical Transactions of the Royal Society of London. Series A: Mathematical,*
398 *Physical and Engineering Sciences*, 361(1810), 1977–1999.
- 399 Beauchamp, J. J., & Olson, J. S. (1973). Corrections for bias in regression estimates
400 after logarithmic transformation. *Ecology*, 54(6), 1403–1407.
- 401 Bol, R., Henson, S. A., Rumyantseva, A., & Briggs, N. (2018). High-frequency
402 variability of small-particle carbon export flux in the northeast atlantic. *Global*
403 *Biogeochemical Cycles*, 32(12), 1803–1814.
- 404 Brzezinski, M. A., Olson, R. J., & Chisholm, S. W. (1990). Silicon availability and
405 cell-cycle progression in marine diatoms. *Marine ecology progress series*, 83–
406 96.
- 407 Buitenhuis, E. T., Le Quere, C., Bednaršek, N., & Schiebel, R. (2019). Large con-
408 tribution of pteropods to shallow caco₃ export. *Global Biogeochemical Cycles*,
409 33(3), 458–468.
- 410 Cael, B. (2021). Variability-based constraint on ocean primary production models.
411 *Limnology and Oceanography Letters*, 6(5), 262–269.
- 412 Cael, B., Bisson, K., Conte, M., Duret, M. T., Follett, C. L., Henson, S. A., ...
413 others (2021). Open ocean particle flux variability from surface to seafloor.
414 *Geophysical Research Letters*, 48(9), e2021GL092895.
- 415 Cael, B., Bisson, K., & Follett, C. L. (2018). Can rates of ocean primary production
416 and biological carbon export be related through their probability distributions?
417 *Global biogeochemical cycles*, 32(6), 954–970.
- 418 Campbell, J. W. (1995). The lognormal distribution as a model for bio-optical vari-
419 ability in the sea. *Journal of Geophysical Research: Oceans*, 100(C7), 13237–
420 13254.
- 421 Cram, J. A., Weber, T., Leung, S. W., McDonnell, A. M., Liang, J.-H., & Deutsch,
422 C. (2018). The role of particle size, ballast, temperature, and oxygen in the
423 sinking flux to the deep sea. *Global Biogeochemical Cycles*, 32(5), 858–876.
- 424 Ducklow, H. W., Steinberg, D. K., & Buesseler, K. O. (2001). Upper ocean carbon
425 export and the biological pump. *Oceanography*, 14(4), 50–58.
- 426 Efron, B., & Tibshirani, R. (1986). Bootstrap methods for standard errors, confi-
427 dence intervals, and other measures of statistical accuracy. *Statistical science*,
428 54–75.
- 429 Francois, R., Honjo, S., Krishfield, R., & Manganini, S. (2002). Factors controlling
430 the flux of organic carbon to the bathypelagic zone of the ocean. *Global Bio-*
431 *geochemical Cycles*, 16(4), 34–1.
- 432 Friedlingstein, P., O’Sullivan, M., Jones, M. W., Andrew, R. M., Gregor, L., Hauck,
433 J., ... others (2022). Global carbon budget 2022. *Earth System Science Data*,
434 14(11), 4811–4900.
- 435 Garcia, H., Weathers, K., Paver, C., Smolyar, I., Boyer, T., Locarnini, M., ... oth-
436 ers (2019). World ocean atlas 2018. vol. 4: Dissolved inorganic nutrients
437 (phosphate, nitrate and nitrate+ nitrite, silicate).

- Gnanadesikan, A. (1999). A global model of silicon cycling: Sensitivity to eddy parameterization and dissolution. *Global Biogeochemical Cycles*, 13(1), 199–220.
- Griffiths, J. D., Barker, S., Hendry, K. R., Thornalley, D. J., Van De Flierdt, T., Hall, I. R., & Anderson, R. F. (2013). Evidence of silicic acid leakage to the tropical atlantic via antarctic intermediate water during marine isotope stage 4. *Paleoceanography*, 28(2), 307–318.
- Heinze, C., Eyring, V., Friedlingstein, P., Jones, C., Balkanski, Y., Collins, W., ... others (2019). ESD reviews: Climate feedbacks in the earth system and prospects for their evaluation. *Earth System Dynamics*, 10(3), 379–452.
- Henson, S. A., Laufkötter, C., Leung, S., Giering, S. L., Palevsky, H. I., & Cavan, E. L. (2022). Uncertain response of ocean biological carbon export in a changing world. *Nature Geoscience*, 15(4), 248–254.
- Henson, S. A., Sanders, R., & Madsen, E. (2012). Global patterns in efficiency of particulate organic carbon export and transfer to the deep ocean. *Global Biogeochemical Cycles*, 26(1).
- Holzer, M., Primeau, F. W., DeVries, T., & Matear, R. (2014). The southern ocean silicon trap: Data-constrained estimates of regenerated silicic acid, trapping efficiencies, and global transport paths. *Journal of Geophysical Research: Oceans*, 119(1), 313–331.
- Klaas, C., & Archer, D. E. (2002). Association of sinking organic matter with various types of mineral ballast in the deep sea: Implications for the rain ratio. *Global biogeochemical cycles*, 16(4), 63–1.
- Kwon, E. Y., Primeau, F., & Sarmiento, J. L. (2009). The impact of remineralization depth on the air–sea carbon balance. *Nature Geoscience*, 2(9), 630–635.
- Le Quéré, C., Buitenhuis, E. T., Moriarty, R., Alvain, S., Aumont, O., Bopp, L., ... others (2016). Role of zooplankton dynamics for southern ocean phytoplankton biomass and global biogeochemical cycles. *Biogeosciences*, 13(14), 4111–4133.
- Malviya, S., Scalco, E., Audic, S., Vincent, F., Veluchamy, A., Poulain, J., ... others (2016). Insights into global diatom distribution and diversity in the world’s ocean. *Proceedings of the National Academy of Sciences*, 113(11), E1516–E1525.
- Marsay, C. M., Sanders, R. J., Henson, S. A., Pabortsava, K., Achterberg, E. P., & Lampitt, R. S. (2015). Attenuation of sinking particulate organic carbon flux through the mesopelagic ocean. *Proceedings of the National Academy of Sciences*, 112(4), 1089–1094.
- Martin, J. H., Knauer, G. A., Karl, D. M., & Broenkow, W. W. (1987). Vertex: carbon cycling in the northeast pacific. *Deep Sea Research Part A. Oceanographic Research Papers*, 34(2), 267–285.
- Martin-Jézéquel, V., Hildebrand, M., & Brzezinski, M. A. (2000). Silicon metabolism in diatoms: implications for growth. *Journal of phycology*, 36(5), 821–840.
- Matsumoto, K., & Sarmiento, J. L. (2008). A corollary to the silicic acid leakage hypothesis. *Paleoceanography*, 23(2).
- Matsumoto, K., Sarmiento, J. L., & Brzezinski, M. A. (2002). Silicic acid leakage from the southern ocean: A possible explanation for glacial atmospheric pco₂. *Global Biogeochemical Cycles*, 16(3), 5–1.
- Mouw, C. B., Barnett, A., McKinley, G. A., Gloege, L., & Pilcher, D. (2016). Global ocean particulate organic carbon flux merged with satellite parameters. *Earth System Science Data*, 8(2), 531–541.
- Pančić, M., Torres, R. R., Almeda, R., & Kjørboe, T. (2019). Silicified cell walls as a defensive trait in diatoms. *Proceedings of the Royal Society B*, 286(1901), 20190184.
- Parekh, P., Follows, M. J., Dutkiewicz, S., & Ito, T. (2006). Physical and biological regulation of the soft tissue carbon pump. *Paleoceanography*, 21(3).
- Petrou, K., Baker, K. G., Nielsen, D. A., Hancock, A. M., Schulz, K. G., & David-

- son, A. T. (2019). Acidification diminishes diatom silica production in the southern ocean. *Nature Climate Change*, 9(10), 781–786.
- Pondaven, P., Gallinari, M., Chollet, S., Bucciarelli, E., Sarthou, G., Schultes, S., & Jean, F. (2007). Grazing-induced changes in cell wall silicification in a marine diatom. *Protist*, 158(1), 21–28.
- Qiu, B., & Huang, R. X. (1995). Ventilation of the north atlantic and north pacific: subduction versus obduction. *Journal of Physical Oceanography*, 25(10), 2374–2390.
- Round, F. E., Crawford, R. M., & Mann, D. G. (1990). *Diatoms: biology and morphology of the genera*. Cambridge university press.
- Ryderheim, F., Grønning, J., & Kiørboe, T. (2022). Thicker shells reduce copepod grazing on diatoms. *Limnology and Oceanography Letters*.
- Sarmiento, J. L., Gruber, N., Brzezinski, M., & Dunne, J. (2004). High-latitude controls of thermocline nutrients and low latitude biological productivity. *Nature*, 427(6969), 56–60.
- Sarmiento, J. L., Simeon, J., Gnanadesikan, A., Gruber, N., Key, R., & Schlitzer, R. (2007). Deep ocean biogeochemistry of silicic acid and nitrate. *Global Biogeochemical Cycles*, 21(1).
- Siegel, D., DeVries, T., Doney, S., & Bell, T. (2021). Assessing the sequestration time scales of some ocean-based carbon dioxide reduction strategies. *Environmental Research Letters*, 16(10), 104003.
- Tréguer, P., Bowler, C., Moriceau, B., Dutkiewicz, S., Gehlen, M., Aumont, O., ... others (2018). Influence of diatom diversity on the ocean biological carbon pump. *Nature Geoscience*, 11(1), 27–37.
- Wilson, J. D., Barker, S., & Ridgwell, A. (2012). Assessment of the spatial variability in particulate organic matter and mineral sinking fluxes in the ocean interior: Implications for the ballast hypothesis. *Global Biogeochemical Cycles*, 26(4).
- Wright, R. M., Le Quéré, C., Buitenhuis, E., Pitois, S., & Gibbons, M. J. (2021). Role of jellyfish in the plankton ecosystem revealed using a global ocean biogeochemical model. *Biogeosciences*, 18(4), 1291–1320.