# S1 Introduction

This supplementary information comprises detailed descriptions of the Biogeochemical Reaction Network Simulator (BRNS), adapted for the benthic silica cycle and of the proposed Barents Sea Si budget. Here we also present additional model output figures, including the best-fit steady state simulation for station B14 and alternative fits for stations B13 and B15, wherein a heavier isotopic composition of the silicon (Si) phase desorbing from solid iron (Fe) (oxyhydr)oxides can reproduce the subtle continued increase in sediment pore water dissolved silicic acid (DSi) concentrations with depth.

# S2 Biogeochemical Reaction Network Simulator

## S2.1 Steady state model description

Reaction-transport models (RTMs) simulate and disentangle the complex interplay of chemical reactions and transport processes in sediments. Through use of an array of boundary conditions, a virtual sediment core can be placed in a real world context and used to fit laboratory data, from which it becomes possible to discern further information from concentration and isotopic measurements. For the early diagenesis of silica, this can prove useful as RTMs allow for the quantification of precipitation and dissolution reaction pathways, which can be difficult to constrain. Data-model best-fits were obtained by minimising RMSE (equation S1) between the predicted and observed values (Table S1).

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(x_i - x_i)^2} \tag{S1}$$

where $i$ refers to variable i, $n$ is the number of data points, $x_i$ is the observational data and $x_i$ represents the simulated data.

The Biogeochemical Reaction Network Simulator (BRNS) is an adaptive simulation environment suitable for large, mixed kinetic-equilibrium reaction networks (Regnier et al., 2002; Aguilera et al., 2005). A comprehensive list of boundary conditions and model parameters can be found in Table S2. This model assumes a steady state depositional dynamic and therefore cannot resolve seasonal or transient dynamics. BRNS is based on the vertically-resolved mass conservation equation S2 (Boudreau, 1997), which simulates concentration changes for solid and dissolved species ($i$) in porous media at each depth interval and time step:

$$\frac{\delta \sigma C_i}{\delta t} = \frac{\delta}{\delta z}\left(D_{bio}\sigma\frac{\delta C_i}{\delta z} + D_i\sigma\frac{\delta C_i}{\delta z}\right) - \frac{\delta \sigma \omega C_i}{\delta z} + \alpha_i \sigma(C_i(0) - C_i) + \sum_j \lambda_i^j R_j, \tag{S2}$$

where $\omega$, $C_i$, $t$ and $z$ represent the sedimentation rate, concentration of species $i$, time and depth respectively. The porosity term $\sigma$ is given as $\sigma = (1 - \varphi)$ for solid species, whereas for dissolved species $\sigma = \varphi$, where $\varphi$ is sediment porosity. This term ensures that the respective concentrations represent the amount or mass per unit volume of porewater or solids as required (Boudreau, 1997). Porosity is attenuated exponentially with depth to account for sediment compaction, following (Mogollón et al., 2012):

$$\varphi_z = \varphi_x + (\varphi_0 - \varphi_x)e^{-z\cdot\beta}, \tag{S3}$$

where $\varphi_z$ and $\varphi_0$ is the porosity at depth $z$ and the surface respectively, $\varphi_x$ refers to porosity at depth and $\beta$ is the attenuation coefficient. $\varphi_0$ and $\varphi_x$ were determined for each core and depth interval of Barents Sea sediments alongside this study and values for $\beta$ were established based on best-fits of equation S3 to that data. $D_{bio}$ is the bioturbation coefficient, which is modelled as a diffusive process (cm$^2$ yr$^{-1}$) and was determined experimentally for ChAOS stations along with the maximum

**Table S1.** Goodness of fit measures between observational and simulated data. RMSE given in $\mu$M and ‰ for DSi and $\delta^{30}$Si respectively. Normalised RMSE (NRMSE) is dimensionless, calculated by dividing RMSE by the difference between the maximum and minimum values.

| | **B13** | | | **B14** | | | **B15** | | |
|---|---|---|---|---|---|---|---|---|---|
| | RMSE | NRMSE | $r^2$ | RMSE | NRMSE | $r^2$ | RMSE | NRMSE | $r^2$ |
| DSi | 13.9 | 0.12 | 0.73 | 19.0 | 0.16 | 0.67 | 10.8 | 0.12 | 0.84 |
| $\delta^{30}$Si | 0.16 | 0.12 | 0.83 | 0.30 | 0.13 | 0.87 | 0.21 | 0.11 | 0.60 |

depth of mixing (4.9 ±1.4 cm at B13 and B14; 6.4 ±1.6 cm at B15) (Solan et al., 2020). $D_i$ is the effective molecular diffusion
35  coefficient ($D_i = 0$ for solids) for dissolved species $i$. $D_i$ values for $^{28}Si$ and $^{30}Si$ measured in 2$^o$C seawater were taken from Rebreanu et al. (2008) and corrected for sediment tortuosity ($\theta^2$) to produce $D_{sed}$ (Boudreau, 1996). D$_i$ varies with temperature (T) and viscosity ($\eta$), which was calculated with equation S4 (Rebreanu et al., 2008), using core top water temperatures measured at each station.

$$D_{sw} = 3.33 \times 10^{-12} \cdot (T / \eta) \tag{S4}$$

40  Sedimentation rate ($\omega$) is relatively poorly constrained in the Barents Sea (Freitas et al., 2020), with estimates ranging from 0.04-2.1 mm yr$^{-1}$ based on $^{14}$C (10-50 cm), $^{210}$Pb and $^{137}$Cs ($\leq$20 cm below the seafloor) analysis (Knies and Stein, 1998; Elverhøi, 1984; Elverhøi and Solheim, 1983; Zaborska et al., 2008; Carroll et al., 2008; Smith et al., 1995; Maiti et al., 2010; Faust et al., 2020). Given that measurements of DSi concentration and the isotopic compositions were determined only in the upper 30 cm of seafloor sediment, here we utilise $^{210}$Pb sedimentation rate estimates from stations largely consistent with the
45  localities of B13, B14 and B15.

Unlike for bioturbation, the bioirrigation rate ($\alpha_i$, yr$^{-1}$) for dissolved species ($\alpha_i = 0$ for solid species) was not experimentally determined alongside this study. Instead we implement a global mean value for the coefficient itself and also for its attenuation depth ($x_{irr}$) (Freitas et al., 2020; Thullner et al., 2009). We assume an attenuation depth of 3.5 cm, which typically irrigates sediment down to 15 cm depth (Thullner et al., 2009). The bioirrigation rate is determined from the coefficient applied
50  at the surface (equation S5) and describes exchange between the sediment-water interface (SWI) and the pore water below, which is defined as a 'nonlocal' process, i.e. transport of material occurs between points that are not adjacent to eachother (Boudreau, 1997). $\sum\limits_{j} R_j$ represents the sum of the reactions ($j$) of reaction rate $R_j$ within the implemented network that are either consuming or producing species $i$, while $\lambda_i^j$ is the stoichiometric coefficient of species $i$ for reaction $j$.

$$\alpha = \alpha_0 \cdot e^{\left(\frac{-z}{x_{irr}}\right)} \tag{S5}$$

55  Mass conservation equation S2 is discretised spatially through use of a one dimensional finite-differencing mechanism (Thullner et al., 2009) over an irregular grid of 101 nodes (Boudreau, 1997), representing 50.4 cm of sampled core depth. Depth intervals are resolved at 0.1 cm to 3 cm depth, 0.2 cm to 5 cm, 0.4 cm to 10 cm, 0.6 cm to 20 cm and finally 1 cm intervals to 50 cm below the seafloor.

To summarise, equation S2 simulates concentration changes for solid and dissolved species in porous media at each depth
60  interval and time step, caused by multiple processes, including: sediment accumulation and compaction, molecular diffusion, macroinfaunal mixing (bioturbation and bioirrigation) and the consumption or production of species as defined by the user implemented reaction network.

## S2.2 Reaction network and isotopic fractionation

The version of Si-BRNS employed in this study is similar to that found in Cassarino et al. (2020), which largely follows the
approach of Ehlert et al. (2016). The model accounts for a pool of sediment pore water DSi (as $DSi_{30}$ and $DSi_{28}$) and biogenic
silica (as $BSi_{30}$ and $BSi_{28}$). We assume that the total abundnace of Si is accounted for by $Si_{30}$ and $Si_{28}$ (95.3%). In order to
simulate the isotopic fractionation of Si due to early diagenetic processes, the model upper boundary conditions (at the SWI)
require the concentration of the isotopes $^{28}Si$ and $^{30}Si$ in mol cm$^{-3}$ of the implemented phases. Through the measured isotopic
composition of the modelled phases and the abundance ratios of the NBS-28 reference standard ($[Si_{29}]/[Si_{28}]$ = 0.050745
and $[Si_{30}]/[Si_{28}]$ = 0.034147, Ding et al. (2005)), it is possible to calculate the same ratios of the analysed material through
rearrangement of equation S6 (see equations S7 and S8). Subsequently, the concentration of each individual Si isotope was
calculated through a series of mass balance equations (equations S9-S12), which were used as upper boundary concentrations.
A no-flux condition was imposed for all species at the lower boundary of the model environment ($\delta C_i/\delta z = 0$), thereby
assuming that biogeochemical processes at greater depth do not influence the modelled domain.

$$\delta^{30}Si = \left( \frac{(^{30}Si/^{28}Si)_{sample}}{(^{30}Si/^{28}Si)_{NBS-28}} - 1 \right) \cdot 1000 \tag{S6}$$

$$\frac{[Si_{29}]}{[Si_{28}]}_{sample} = \left( \frac{\delta^{29}Si_{sample}}{1000} + 1 \right) \cdot \frac{[Si_{29}]}{[Si_{28}]}_{standard} \tag{S7}$$

$$\frac{[Si_{30}]}{[Si_{28}]}_{sample} = \left( \frac{\delta^{30}Si_{sample}}{1000} + 1 \right) \cdot \frac{[Si_{30}]}{[Si_{28}]}_{standard} \tag{S8}$$

$$\frac{[Si_{28}]}{[Si_{tot}]} + \frac{[Si_{29}]}{[Si_{tot}]} + \frac{[Si_{30}]}{[Si_{tot}]} = 1 \tag{S9}$$

$$\frac{\frac{[Si_{28}]}{[Si_{tot}]} + \frac{[Si_{29}]}{[Si_{tot}]} + \frac{[Si_{30}]}{[Si_{tot}]}}{[Si_{28}]} = \frac{1}{[Si_{28}]} \tag{S10}$$

$$\therefore [Si_{28}] = \frac{1}{\frac{1}{[Si_{tot}]} + \frac{1}{[Si_{tot}]} \cdot \left( \frac{[Si_{29}]}{[Si_{28}]} + \frac{[Si_{30}]}{[Si_{28}]} \right)} \tag{S11}$$

$$\therefore [Si_{29}] = [Si_{tot}] - [Si_{28}] - \left( [Si_{28}] \cdot \frac{[Si_{30}]}{[Si_{28}]} \right) \tag{S12}$$

Following Ehlert et al. (2016) and Cassarino et al. (2020), the model used in this study accounts for a pool of pore water
DSi, sourced by a dissolving biogenic phase (BSi), from which Si can be incorporated into authigenic clay minerals as they
precipitate (AuSi$_{30}$ and AuSi$_{28}$), thereby inducing a fractionation on the DSi phase. The Si isotopic fractionation factor ($^{30}\epsilon$)
associated with AuSi precipitation is relatively high (-1.8 to -2.2 ‰) (Hughes et al., 2013; Ziegler et al., 2005a, b; Opfergelt
and Delmelle, 2012). The kinetic rate law for the dissolution of BSi follows equation S16 (Hurd, 1972), where $k_{diss}$ is the
reaction rate constant (yr$^{-1}$) and $BSi_{sol}$ is the solubility of BSi (mol cm$^{-3}$), therefore stating that the rate is proportional

to the saturation state of the DSi phase. The rate of BSi dissolution is allowed to decrease exponentially downcore following equation S15, where $ad$ is the attenuation coefficient and $bd$ is the minimum reaction rate, in order to account for a reduction in reactivity due to maturation and interaction with dissolved Aluminium (Al), as well as the preferential dissolution of more reactive material at shallower depths (Rickert, 2000; Van Cappellen and Qiu, 1997; Rabouille et al., 1997; Dixit et al., 2001). While this study assumed that no isotopic fractionation occurs during BSi dissolution ($\alpha_d$ = 1.0) (Wetzel et al., 2014; Ehlert et al., 2016), equations S17 and S18 allow for an equilibrium fractionation to be induced if required, through use of the fractionation factor $\alpha_d$. Indeed, previous work has shown that BSi dissolution can sometimes induce a slight fractionation that enriches the DSi pool in the lighter isotope ($^{30}\epsilon$ of -0.55 ‰) (Demarest et al., 2009).

$$fb_{30} = \frac{BSi_{30}}{BSi_{30} + \alpha_d \cdot BSi_{28}} \tag{S13}$$

$$fb_{28} = \frac{\alpha_d \cdot BSi_{28}}{BSi_{30} + \alpha_d \cdot BSi_{28}} \tag{S14}$$

$$fb_z = e^{-ad \cdot x_{pos}} + bd \tag{S15}$$

$$R_{db} = k_{diss} \cdot fb_z \cdot (BSi_{30} + BSi_{28}) \cdot \left(1.0 - \frac{(DSi_{30} + DSi_{28})}{BSi_{sol}}\right) \tag{S16}$$

$$R_2 = fb_{30} \cdot R_{db} \tag{S17}$$

$$R_3 = fb_{28} \cdot R_{db} \tag{S18}$$

An additional two reaction pathways have been introduced into our model relative to those of Cassarino (2018) and Ehlert et al. (2016)- the dissolution of a lithogenic phase ($LSi_{30}$ and $LSi_{28}$) and two reaction rates representing the release of $DSi_{30}$ and $DSi_{28}$ from solid phase Fe (oxyhydr)oxides. As for BSi, LSi dissolution is assumed to be dependent upon the degree of pore water DSi undersaturation and follows equation S20, where $k_{LSidiss}$ is the dissolution rate constant and $LSi_{sol}$ represents the solubility of the lithogenic phase. Lerman et al. (1975) determined during a dissolution experiment of common silicate minerals that the reaction could be described by a first-order rate law, driven by the saturation state. The concentration of LSi ($LSi_{28}$ and $LSi_{30}$) was determined based on sedimentary bulk Si contents measured by wavelength dispersive X-ray fluorescence (XRF) of the 0-0.25 cm sediment core depth interval: 26.1, 24.7 and 23.3 % Si at stations B13, B14 and B15 respectively. For XRF analysis, sample splits of 700 mg was mixed with 4200 mg di-lithiumtetraborate (Li2B4O7, Spectromelt A10), preoxidized at 500°C with 1.0 g $NH_4NO_3$ (p.a.) and fused to homogenous glass beads. The glass beads were analysed using a Philips PW-2400 WD-XRF spectrometer calibrated with 53 geostandards at the University of Oldenburg. Analytical precision and accuracy were better than 5%, as checked by in-house and international reference materials. Bulk sediment Si contents were then corrected for the BSi component, assuming that almost all of the solid phase is composed of terrigenous material. Ward et al. (in revision) determined that approximately 96% of Barents Sea surface sediments are terrigenous in origin, calculated using equation S21 (Sayles et al., 2001).

The LSi dissolution rate is set to decrease exponentially with depth, following equation S19, where $al$ is the attenuation coefficient, $bl$ represents the minimum rate and $x_{pos}$ is depth. This exponential reduction in rate is imposed because the uppermost sediment layers are thought to be where the majority of dissolved Al sourced from LSi dissolution is released in marine sediments (Van Beusekom et al., 1997; Ehlert et al., 2016; Geilert et al., 2020). We have assumed there is no isotopic fractionation during the dissolution of LSi.

$$fl_z = e^{-al \cdot x_{pos}} + bl \tag{S19}$$

$$R_{dl} = k_{LSidiss} \cdot fl_z \cdot (LSi_{30} + LSi_{28}) \cdot \left( 1.0 - \frac{(DSi_{30} + DSi_{28})}{LSi_{sol}} \right) \tag{S20}$$

$$\%Terrigenous = 100 - \%(BSi + CaCO_3 + TOC) \tag{S21}$$

where TOC refers to total organic carbon content of the surface sediment interval.

The desorption of DSi from solid phase Fe (oxyhydr)oxides as they reductively dissolve under anoxic conditions was modelled through two reaction rate constants, representing the release of $DSi_{30}$ ($k_{FeSi30}$) and $DSi_{28}$ ($k_{FeSi28}$) from the solid phase (equations S22-S23). This parameter likely represents a significant simplification, however the exact process pertaining to the adsorption of Si onto Fe (oxyhydr)oxides is unclear and requires further study (Geilert et al., 2020). Adsorption of Si onto Fe (oxyhydr)oxides preferentially takes up the lighter isotope, the degree to which is thought to increase with mineral crystallinity ($^{30}\epsilon$ of -1.06 ‰ for ferrihydrite and -1.59 ‰ for goethite) (Delstanche et al., 2009). Furthermore, Ward et al. (in revision) presented evidence for the presence of an isotopically light metal oxide phase, through analysis of weak acid leachates used to extract solid phase reactive Si pools (-2.88 ±0.17 ‰). The implemented ratio of $k_{FeSi30}$ and $k_{FeSi28}$ in the model reflects the composition of this reactive pool.

Step-functions (SW03 and SW04) were implemented in the FeSi reactions in the model to simulate the desorption of this phase at specific depth intervals, representing the Fe redox boundaries identified in Ward et al. (under revision). The step-functions act as a cut-off mechanism, either setting reaction rates to zero or activating them at specific depths. Release of the FeSi phase was ceased at a particular depth interval, determined based on the best-fit between the simulated and measured data.

$$R_7 = SW03 \cdot SW04 \cdot k_{FeSi28} \tag{S22}$$

$$R_8 = SW03 \cdot SW04 \cdot k_{FeSi30} \tag{S23}$$

The precipitation of authigenic clay minerals ($AuSi_{30}$ and $AuSi_{28}$) was modelled with equation S27, where $k_{precip}$ represents the authigenic rate constant (Ehlert et al., 2016). This rate law states, through use of a step-function ($SW02$), that the reaction will proceed, providing the concentration of DSi is greater than the solubility of the authigenic phase ($AuSi_{sol}$). The rate is thus proportional to the degree of pore water DSi oversaturation (Ehlert et al., 2016). As with BSi dissolution, the rate of AuSi precipitation was allowed to decrease exponentially with depth through equation S26, where $ap$ is the attenuation coefficient and $bp$ is the minimum rate. This reduction in reaction rate with depth accounts for the general consensus that the majority of authigenic clay mineral precipitation occurs in the upper portion of marine sediment cores. Here, DSi can more easily precipitate in the presence of dissolved Al, the concentration of which is typically higher in the upper reaches of shelf

sediments, sourced from the dissolution of reactive LSi minerals (e.g. feldspar and gibbsite) contemporaneous to that of BSi
150 (Aller, 2014; Rabouille et al., 1997; Van Beusekom et al., 1997; Ehlert et al., 2016). Fractionation of the dissolved phase
associated with clay mineral precipitation is accounted for by equations S28 and S29, through the fractionation factor $\alpha_p$.

$$fp_{30} = \frac{DSi_{30}}{DSi_{30} + \alpha_p \cdot DSi_{28}} \tag{S24}$$

$$fp_{28} = \frac{\alpha_p \cdot DSi_{28}}{DSi_{30} + \alpha_p \cdot DSi_{28}} \tag{S25}$$

$$fp_z = e^{-ap \cdot x_{pos}} + bp \tag{S26}$$

155 $$R_p = SW02 \cdot k_{precip} \cdot fp_z \cdot \left( \frac{(DSi_{30} + DSi_{28})}{AuSi_{sol} - 1.0} \right) \qquad \text{if [DSi]} > AuSi_{sol} \tag{S27}$$

$$R_{10} = fp_{30} \cdot R_p \tag{S28}$$

$$R_{11} = fp_{28} \cdot R_p \tag{S29}$$

Table S2: BRNS transport and reaction parameters and boundary conditions. Values are 'independent' (I) if based on laboratory or field estimation, 'constrained' (C) if potential values could be bracketed or calculated from an empirical relationship, or finally 'model-derived' (M). *Lerman et al. (1975) determined that glauconite, a common aluminosilicate reverse weathering product of BSi has a solubility of $\sim$50 $\mu$M in seawater at low temperatures. Hurd (1973) calculated that sepiolite, an authigenic clay mineral that forms on BSi could precipitate from sediment pore waters with a DSi as low as 30 $\mu$M. [†] Zhu et al. (2016) observed fractionation factors ($^{30}\epsilon$) of -2.87 to +0.80 ‰, averaging -0.995 $\pm$1.16 ‰ (1$\sigma$) during albite dissolution, with the DI water solution becoming enriched in the lighter isotope. However, the magnitude of $^{30}\epsilon$ was found to be dependent on pH and was much lower at pH 7 (averaging 0.11 $\pm$0.98 ‰).

| Parameter | Unit | Type | B13 | B14 | B15 | Source |
|---|---|---|---|---|---|---|
| *General* | | | | | | |
| L | cm | - | 50.4 | 50.4 | 50.4 | - |
| nNodes | - | - | 101 | 101 | 101 | - |
| Run time | yr | - | 2600 | 3000 | 3000 | - |
| T | $^{o}C$ | I | 1.78 | 1.9 | -1.49 | - |
| S | PSU | I | 35.014 | 35.01 | 35.9 | - |
| Depth | m | I | 359 | 293 | 317 | - |
| $\varphi_0$ | - | I | 0.83 | 0.89 | 0.90 | - |
| $\varphi_x$ | - | I | 0.62 | 0.65 | 0.65 | - |
| $\beta$ | - | I | 0.10 | 0.105 | 0.105 | - |
| *Transport* | | | | | | |
| $D_{bio}$ | cm$^2$ yr$^{-1}$ | I | 6.1 | 3.9 | 1.9 | - |
| $x_{bio}$ | cm | I | 2.0 | 2.0 | 2.0 | - |
| $\alpha_0$ | yr$^{-1}$ | C | 10 | 10 | 10 | Thullner et al. (2009) |
| $x_{irr}$ | cm | C | 3.5 | 3.5 | 3.5 | Thullner et al. (2009) |
| $\omega$ | cm yr$^{-1}$ | C | 0.05 | 0.05 | 0.06 | Zaborska et al. (2008) |
| $D_{sed^{28}Si}$ | cm$^2$ yr$^{-1}$ | C | 125 | 127 | 128 | Rebreanu et al. (2008) |
| $D_{sed^{30}Si}$ | cm$^2$ yr$^{-1}$ | C | 125 | 127 | 128 | Rebreanu et al. (2008) |
| *Reaction* | | | | | | |
| $[DSi_{28}]$ | $\mu$mol Si cm$^{-3}$ | I | 0.00645 | 0.00829 | 0.00553 | - |
| $[DSi_{30}]$ | $\mu$mol Si cm$^{-3}$ | I | 0.00022 | 0.00028 | 0.00019 | - |
| $[BSi_{28}]$ | $\mu$mol Si cm$^{-3}$ solid | I | $3.22 \cdot 10^2$ | $4.27 \cdot 10^2$ | $2.12 \cdot 10^2$ | - |
| $[BSi_{30}]$ | $\mu$mol Si cm$^{-3}$ solid | I | $1.1 \cdot 10^1$ | $1.46 \cdot 10^1$ | 7.23 | - |
| $\delta^{30}Si_{DSi}$ | ‰ | I | 1.64 | 1.46 | 1.69 | - |
| $\delta^{29}Si_{DSi}$ | ‰ | I | 0.84 | 0.8 | 0.89 | - |
| $\delta^{30}Si_{BSi}$ | ‰ | I | 1.43 | 1.5 | 0.82 | - |
| $\delta^{29}Si_{BSi}$ | ‰ | I | 0.71 | 0.76 | 0.39 | - |
| $\delta^{30}Si_{LSi}$ | ‰ | I | -0.89 | -0.89 | -0.89 | - |
| $\delta^{29}Si_{LSi}$ | ‰ | I | -0.49 | -0.49 | -0.49 | - |
| $\delta^{30}Si_{FeSi}$ | ‰ | I | -2.88 | -2.88 | -2.88 | - |

| | | | | | | |
|---|---|---|---|---|---|---|
| $\delta^{29}Si_{FeSi}$ | ‰ | I | -1.46 | -1.46 | -1.46 | - |
| $BSi_{sol}$ | $\mu$M | C | 800 | 800 | 800 | Van Cappellen et al. (2002) |
| $LSi_{sol}$ | $\mu$M | C | 95 | 100 | 95 | See Table S3 |
| $AuSi_{sol}$ | $\mu$M | C | 50 | 50 | 50 | Lerman et al. (1975); Hurd (1973)* |
| $k_{diss}$ | $yr^{-1}$ | M | $0.55 \cdot 10^{-2}$ | $7.4 \cdot 10^{-2}$ | $1.05 \cdot 10^{-2}$ | - |
| $k_{LSidiss}$ | $yr^{-1}$ | M | $200 \cdot 10^{-4}$ | $500 \cdot 10^{-5}$ | $300 \cdot 10^{-5}$ | - |
| $k_{precip}$ | mol Si $cm^{-3}$ $yr^{-1}$ | M | $0.65 \cdot 10^{-4}$ | $0.6 \cdot 10^{-5}$ | $4.5 \cdot 10^{-5}$ | - |
| $k_{FeSi_{28}}$ | mol Si $cm^{-3}$ $yr^{-1}$ | M | $1.44 \cdot 10^{-6}$ | $5.578 \cdot 10^{-8}$ | $5.578 \cdot 10^{-8}$ | - |
| $k_{FeSi_{30}}$ | mol Si $cm^{-3}$ $yr^{-1}$ | M | $4.903 \cdot 10^{-8}$ | $1.899 \cdot 10^{-9}$ | $1.899 \cdot 10^{-9}$ | - |
| $\alpha_d$ | - | C | 1.0 | 1.0 | 1.0 | Wetzel et al. (2014) |
| $\alpha_p$ | - | C | 1.0023 | 1.002 | 1.0023 | Opfergelt and Delmelle (2012) |
| $\alpha_l$ | - | C | 1.0 | 1.0 | 1.0 | Zhu et al. (2016)[†] |
| $ad$ | - | M | 0.2 | 0.42 | 0.4 | - |
| $al$ | - | M | 0.2 | 0.01 | 0.05 | - |
| $ap$ | - | M | 0.65 | 0.85 | 0.35 | - |
| $bd$ | $yr^{-1}$ | M | 0.05 | 0.0 | 0.0 | - |
| $bl$ | $yr^{-1}$ | M | 6.0 | 1.5 | 6.0 | - |
| $bp$ | mol Si $cm^{-3}$ $yr^{-1}$ | M | 0.05 | 0.0065 | 0.0001 | - |

## S3   A proposed Si budget for the Barents Sea

An isotopic assessment of the Arctic Ocean Si budget has highlighted the requirement for an additional sink of light Si, if
isotopic balance is to be attained (Brzezinski et al., 2021). Here we build on this work by combining isotopic analysis of the
water column and the dissolved and solid phases of the sediment (Ward et al. in revision), with reaction-transport modelling
carried out in this study, to present an isotopically balanced Si budget for the Barents Sea that may help to inform the pan-Arctic
Ocean equivalent.

The Si inflow rate from Atlantic Waters crossing the Barents Sea Opening is 0.42 ±0.07 Tmol Si $yr^{-1}$ (Torres-Valdés
et al., 2013), while the outflow rate through the northern openings (the Barents Sea Exit between Novaya Zemlya and Franz
Josef Land, as well as the Franz Victoria Trough (Fig. 1)) estimated here is 0.35 Tmol Si $yr^{-1}$. This outflow was calcu-
lated by integrating the water column DSi depth profiles of the northernmost ChAOS stations (B16 and B17) and similar
profiles measured during the ARK IX/4 cruise on the Barents Sea side of the shelf break (PS27/006-1, PS27/026-1 and
PS27/027-1, Luchetta et al. (2021)). All water column nutrient data for JR16006 (doi:10.5285/b4c1537e-c729-6463-e053-
6c86abc0c7de), JR17006 (doi:10.5285/b62f2d5d-1f40-0c2c-e053-6c86abc0265d) and JR18006 (doi:10.5285/cc1dec98-40b5-
5c51-e053-6c86abc01a6d) is available at the British Oceanographic Data Centre (BODC). The average depth-integrated DSi
concentration (4.8 $\mu$M) was then multiplied by the Barents Sea volumetric outflow rate (2.3 Sv) (Smedsrud et al., 2013). Unlike
the Arctic Ocean as a whole, which is a slight net exporter of Si with respect to the main inflow and outflow water masses
(Brzezinski et al., 2021), the Barents Sea appears to be a slight net importer. However, our calculations are based on DSi water
column profiles sampled from the lesser of two Barents Sea outflow locations. The main outflow gateway, between Novaya
Zemlya and Franz Josef Land, is also north of the oceanic polar front and dominated by the Arctic Water mass (Fig. 1), there-
fore we would not expect a significant difference in DSi water column profiles between the two localities. Nevertheless we
cannot be certain of the Barents Sea Si outflow rate without concentration data from the eastern side of the shelf. Consistent
with the wider Arctic Ocean Si budget, the $\delta^{30}$Si of the core top water from the Arctic (B15) and Atlantic Water (B13) stations,

180 range from +1.64 to +1.69 ‰ (Ward et al. in revision), assumed here to represent the main outflow and inflow water masses respectively.

The riverine DSi influx presented in Fig. 6 ($2580 \times 10^3$ tSiO$_2$ yr$^{-1}$, or 0.044 Tmol Si yr$^{-1}$), represents the sum of the four main rivers draining into the Barents and White Seas, including the Onega, Northern Dvina, Mezen and the Pechora (Gordeev et al., 1996). The estimated average $\delta^{30}$Si of the fluvial flux to the Arctic Ocean is 1.3 $\pm$0.3 ‰, but varies temporally by season

185 and spatially from +0.86 $\pm$0.3 ‰ in the Lena to +1.6 $\pm$0.25 ‰ in the Yenisey River, which flow into the Laptev and Kara Seas respectively (Sun et al., 2018).

The benthic flux of DSi has been recategorised in our budget of the Barents Sea, relative to that of Brzezinski et al. (2021), reflecting the conclusions drawn from our reaction-transport model study. Here we assume that between 60 and 98% of the benthic DSi flux is sourced from the dissolution of LSi, which represents an input of new Si into the Barents Sea Si budget,

190 while the remainder constitutes an internal recycling flux (i.e. the dissolution of BSi). Therefore, the contribution of LSi to the influx of Si to the Barents Sea, assuming an average benthic flux of +0.23 $\pm$0.11 mmol Si m$^{-2}$ d$^{-1}$ and a shelf seafloor area of 1.4 million km$^{-2}$, ranges from 0.07 to 0.115 Tmol Si yr$^{-1}$. A $\delta^{30}$Si of -0.88 ‰ for the dissolving LSi phase is based on a series of sequential digestion experiments carried out on the surface sediment interval collected from stations B13, B14 and B15 (Ward et al. in revision), but can range from -0.90 to +0.73 ‰ across primary silicates (felsic crustal and mafic mantle

195 source rocks) and -2.9 to 0 ‰ for secondary clay minerals (Opfergelt and Delmelle, 2012) (mean -1.07 ‰, Sutton et al. (2018)).

The two outputs in the biogeochemical cycle of Si in the Barents Sea seafloor, outside of the main water mass outflow, are the burial of AuSi and BSi. The burial of BSi (0.0123 Tmol Si yr$^{-1}$) is calculated in section 3.4 of the main text, based on an asymptotic BSi content of 0.2 wt% below the mid-core at all three stations, assumed to be controlled solely by advection due to sediment accumulation (corrected for compaction). The same equation was used to calculate the burial rate of AuSi across

200 the shelf (0.018-0.24 Tmol Si yr$^{-1}$), based on the simulated concentration at the base of the model domain at stations B14 and B15 (0.32 and 4.8 wt% respectively). The AuSi concentration at depth in the model for station B13 (12 wt%) is much higher than that at B14 and B15, consistent with the increased depth-integrated reaction rate (Table 2), corresponding to a burial rate of 0.87 Tmol Si yr$^{-1}$. This AuSi burial rate far outweighs the sum of the inputs to the Barents Sea, which would lead to a significant imbalance in the Si budget if it were considered a reasonable value with which to scale up our calculations.

205 We therefore employ the values at stations B14 and B15 as conservative estimates for AuSi burial in the Barents Sea in our calculations, as B13 likely represents a site of localised, elevated AuSi precipitation. Alternatively, there could be a complexity that our model does not adequately capture for this station, leading to an overestimated AuSi precipitation rate. The $\delta^{30}$Si of the buried BSi phase is assumed to be the same as the composition measured in the surface sediments, determined from sequential digestion experiments (+0.82 to +1.50 ‰, Ward et al. (in revision)). For the mass balance calculations, the composition of the

210 AuSi phase was assumed to be -1.07 ‰, based on the average composition of secondary minerals (Sutton et al., 2018), however this can range from -2.9 to $\sim$0 ‰ (Opfergelt and Delmelle, 2012).

Disregarding the main water mass in and outflows, our Si budget suggests an influx to the Barents Sea of 0.11-0.16 Tmol Si yr$^{-1}$ at -0.39 to +0.08 ‰ and an outflux of 0.03-0.25 Tmol Si yr$^{-1}$ at -0.97 to -0.03 ‰, with the potential for the higher outflux to account for the slight mass imbalance between the water mass inflow and outflow (0.12 Tmol Si yr$^{-1}$). Our Si budget of

215 the Barents Sea therefore demonstrates that through the re-categorisation of the benthic flux term and the introduction of AuSi burial, we are able to achieve isotopic and mass balance.

## S4 Sediment pigment extraction methodology

Samples of surface sediment (2–3 g) were thawed and centrifuged (Eppendorf, 4000 rpm, 5 min, 4 $^o$C) to remove excess water. Sediment was then transferred to a pre-weighed extraction tube to which 3 mL of 100% acetone was added. Extracts were

220 kept on ice and in the dark during extraction. Samples were sonicated (Sonics Vibracell probe, 50 s, 40 W), then left on ice to soak for 1 hr before centrifugation (Eppendorf, 4000 rpm, 5 min, 4 $^o$C), and the supernatant decanted. The procedure was

repeated until extracts appeared colourless. Samples were filtered prior to HPLC (0.2 $\mu$m, 17 mm Teflon syringe filters, DHI, Denmark). Samples were injected on an Agilent 1200 HPLC system running an HPLC method for sedimentary pigments (Airs et al. (2001), Method C). The Agilent 1200 system comprised a G1312A binary pump, a G1376B thermostated autosampler, a thermostated column compartment and a G1315B photodiode array detector. Pigment extracts (80 $\mu$L) were mixed with MilliQ water (8 $\mu$L) in the autosampler and injected onto the HPLC column (2 Waters Spherisorb ODS2 cartridges coupled together, each 150 x 4.6 mm, particle size 3 $\mu$m, protected with a precolumn containing the same phase). Extracts were maintained in the dark at 4 $^oC$ in the autosampler, and were analysed within 24 hr of extraction. Injection of a mixed standard (DHI Denmark) was performed to check pigment resolution prior to analysis of samples. Chlorophyll and its degradation products were quantified according to response factors calculated from injection of standards (DHI, Denmark). For quantification of hydroxychlorophyllone, the response factor for pheophorbide a was used as the two components have similar UV/vis absorbance spectra (Airs et al., 2001), and no standard was available for hydroxychlorophyllone. Selected sediment samples were analysed by LC/MS$^n$ for assignment of components (Airs et al., 2001). LC/MS$^n$ was performed using an Agilent 6330 ion trap mass spectrometer via an atmospheric pressure chemical ionisation (APCI) source. MS settings were as follows: Ionisation mode: positive, drying temperature 350 $^oC$, vaporiser temperature 450 $^oC$, nebuliser pressure 60 PSI, drying gas flow rate 5 L/min. The scan range was m/z 400–1100. Post column addition of acid was used to aid ionisation of metallated components (Airs and Keely, 2000). Components were assigned based on relative retention time, on-line UV/vis spectra, protonated molecule and fragmentation data (Airs et al., 2001).

For schematic Fig. 2 of the main text, we have assumed that a shift from fucoxanthin (fuco)-dominated surface sediments to those containing both fuco and hexanoyoxyfucoxanthin (hex-fuco) represents a switch from diatom to haptophyte-dominated (e.g. *E. huxleyi* or *Phaeocystis*) material. Fuco is the more common of the two and the dominant pigment of diatoms, while hex-fuco is typical of *Phaeocystis* (Antajan et al., 2004). Therefore, the abundance of hex-fuco relative to fuco, can be used as a proxy to determine *Phaeocystis* prevalence (Antajan et al. (2004) and references therein).

Table S3: Solubility of primary and secondary silicates in seawater (SW). The Siever (1968) experiment was carried out in distilled water (DW).

| Mineral | Solubility ($\mu$M) | Source | Conditions |
|---|---|---|---|
| Kaolinite | 67 | Siever (1968) | 25 days, 25$^o$C, DW |
| | 64;83 | Mackenzie et al. (1967) | 375 days, room temp, SW |
| | 50 | Lerman et al. (1975) | 8.5 years, Bermuda SW |
| | 10-300 | Hurd et al. (1979) | 12 weeks, 1-2$^o$C, SW |
| Montmorillonite | 130; 183 | Mackenzie et al. (1967) | |
| | 100 | Fanning and Schink (1969) | 10 months, room temp, SW |
| | 130;166 | Lerman et al. (1975) | |
| | 80-250 | Hurd et al. (1979) | |
| Chlorite | 33 | Mackenzie and Garrels (1965) | 10 months, room temp, SW |
| | 70 | Mackenzie et al. (1967) | |
| | 30 | Fanning and Schink (1969) | |
| | 40-80 | Hurd et al. (1979) | |
| Illite | 95 | Mackenzie et al. (1967) | |
| | 100 | Lerman et al. (1975) | |
| | 40-70 | Hurd et al. (1979) | |
| Muscovite | 127 | Mackenzie et al. (1967) | |
| | 125 | Lerman et al. (1975) | |
| Glauconite | 60 | Mackenzie et al. (1967) | |
| | 50 | Lerman et al. (1975) | |
| Bentonite | 433 | | |
| | 115-340 | Hurd et al. (1979) | |
| Quartz | 100 | Lerman et al. (1975) | |
| Phillipsite | 150 | | |
| Analcite | 100 | | |
| Prehnite | 92 | | |
| Albite | 55-110 | | |
| Hornblende | 50-120 | | |
| Nepheline | 35-75 | | |
| Biotite | 60-120 | | |
| Hypersthene | 200-275 | | |
| Epidote | 150-200 | | |
| Tremolite | 200-275 | | |
| Olivine | 300-700 | | |
| *Bulk sediment* | | | |
| Congo fan | 48 | Loucaides et al. (2010) | 22 months, ocean mooring |
| Mississippi delta | 46;52 | | |
| *Basalt* | | | |

| | | | |
|---|---|---|---|
| River bedload | 103 | Jones et al. (2012) | 9 months, 5$^o$C, SW |
| Estuary sediment | 129 | | |
| Volcanic glass | 90 | Staudigel et al. (1998) | 314 days, room temp, SW |
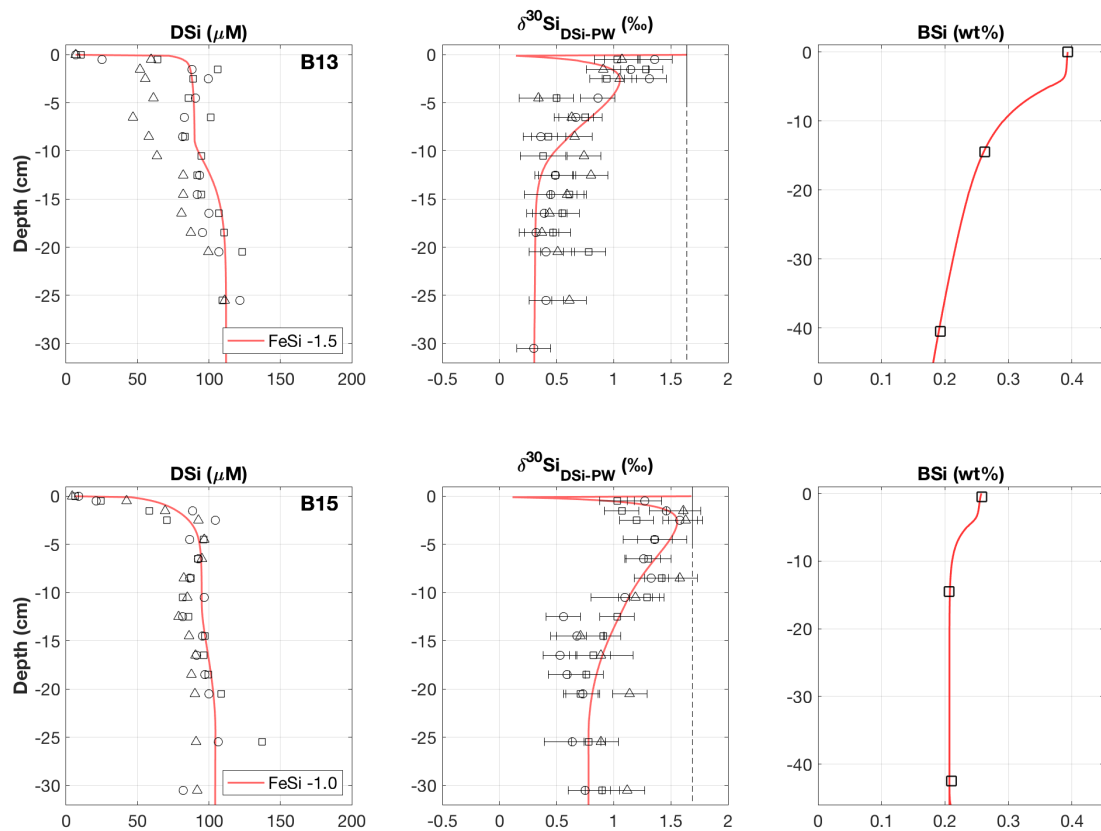
**Figure S1.** Best-fit model simulations (red line) with heavier FeSi compositions of -1.5 and -1.0 ‰ implemented at stations B13 and B15 respectively. The heavier composition of the desorbing phase allows for sufficient DSi release to resolve the slight increase in pore water DSi concentration from the mid-core to depth. Vertical dashed black lines represents the isotopic compositions of the core top waters from 2017.
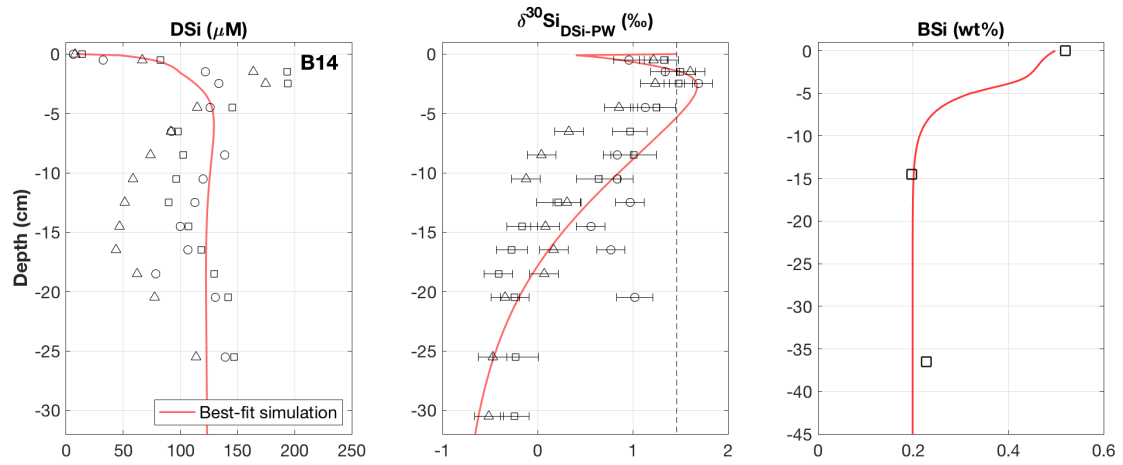
**Figure S2.** Best-fit model simulation station B14 (red line). Vertical dashed black line represents the isotopic composition of the core top water from 2017. BSi content was measured from samples collected in 2019. Model output was fit to the sediment pore water DSi concentrations from 2018 (open circles), as this profile is closer to the background steady state system than 2017 or 2019.
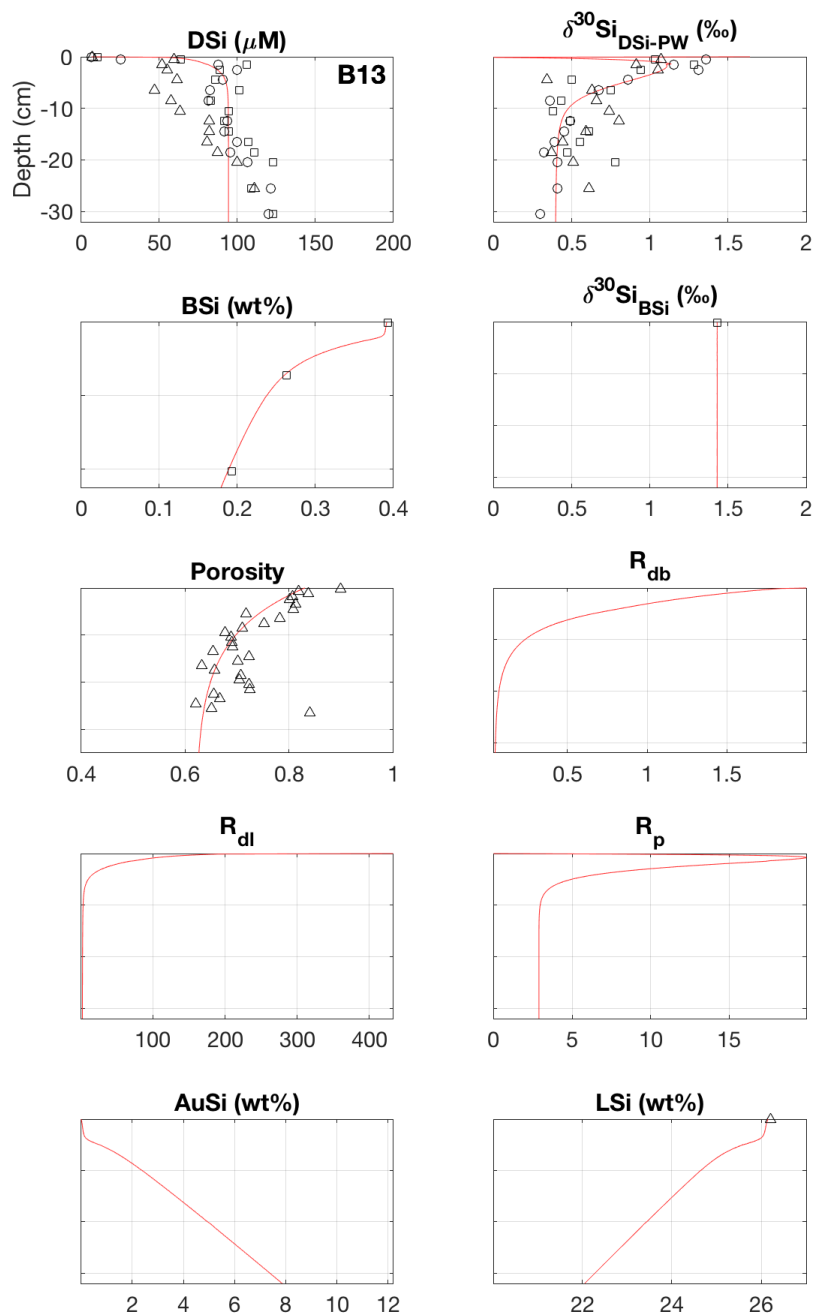
**Figure S3.** Model output summary (red lines) *vs* data (open shapes) from the best-fit simulation at station B13. $R_{db}$- rate of BSi dissolution, $R_{dl}$- rate of LSi dissolution, $R_{p}$- rate of AuSi precipitation. All reaction rates are given in $\mu$mol cm$^{-3}$ yr$^{-1}$.
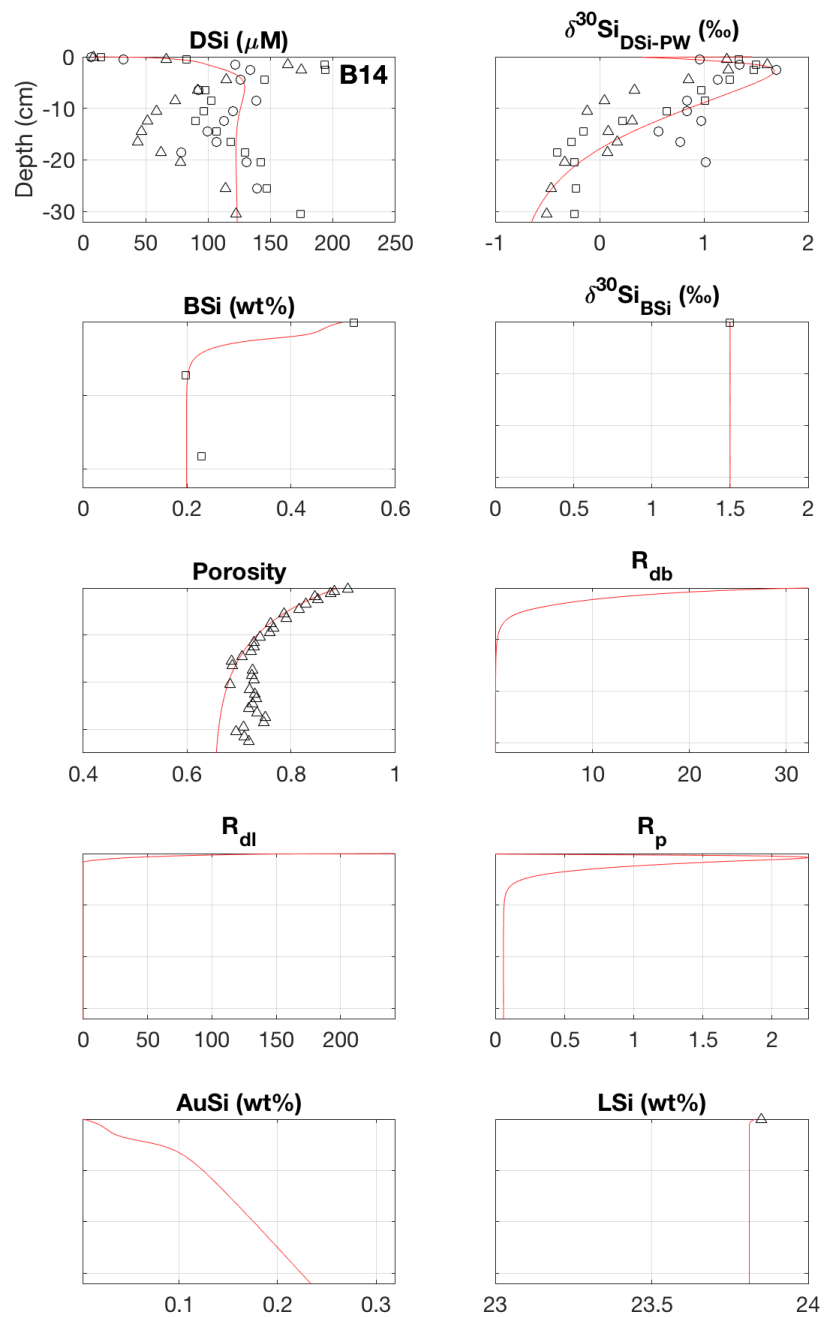
**Figure S4.** Model output summary (red lines) *vs* data (open shapes) from the best-fit simulation at station B14. All reaction rates are given in $\mu$mol cm$^{-3}$ yr$^{-1}$.
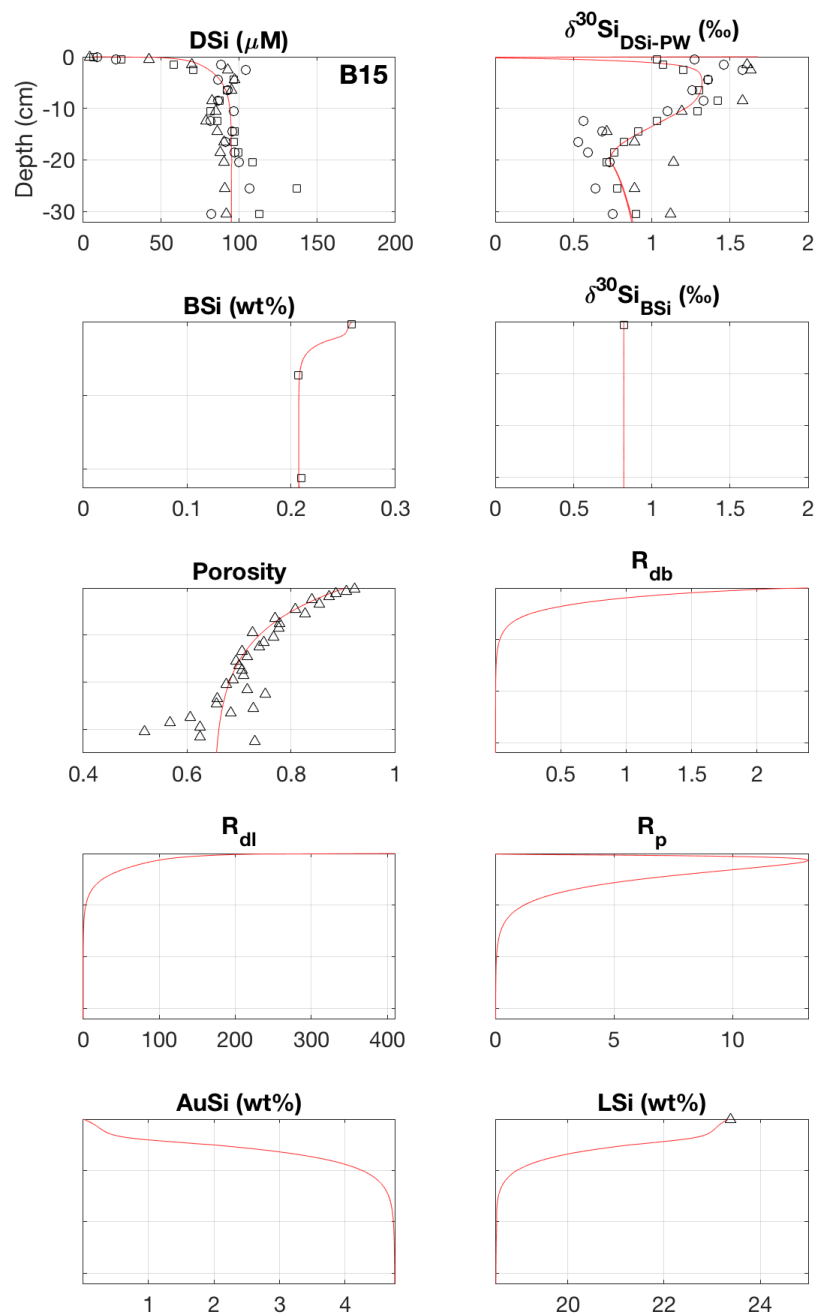
**Figure S5.** Model output summary (red lines) *vs* data (open shapes) from the best-fit simulation at station B15. All reaction rates are given in $\mu$mol cm$^{-3}$ yr$^{-1}$.
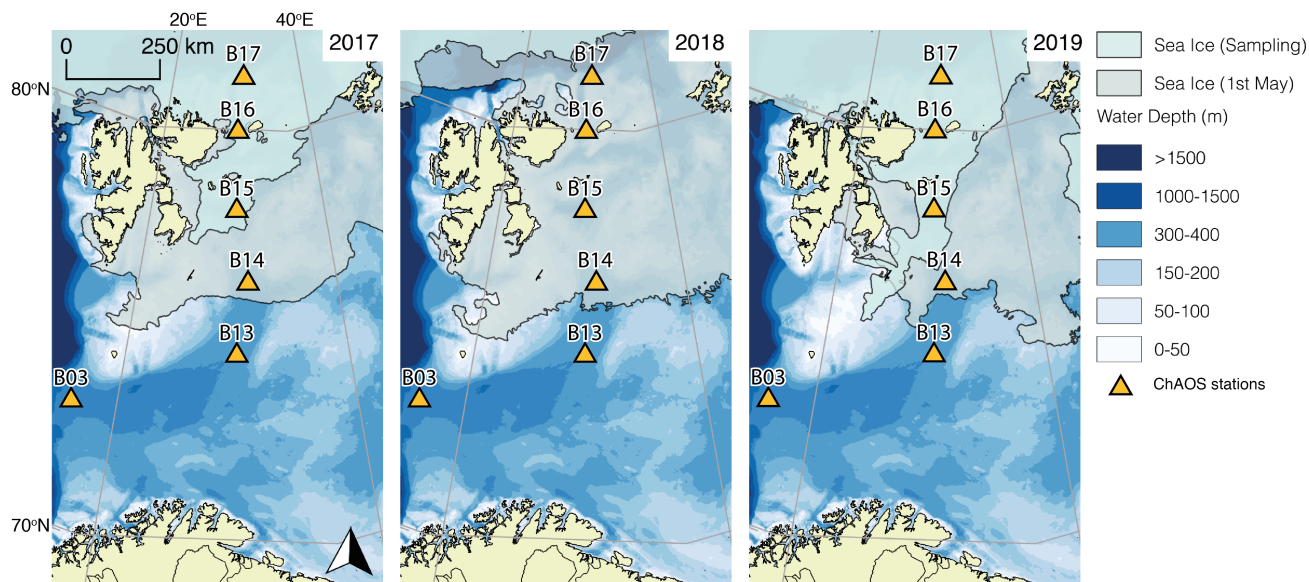
**Figure S6.** Sea ice conditions during sampling at station B14 (30/7/2017, 25/7/2018, 13/7/2019) *vs* May 1st of each year (Ward et al. in revision). Sea ice data from U.S. National Ice Center and National Snow and Ice Data Center (NSIDC) (Fetterer et al., 2010).

*Code and data availability.* Research data associated with this article can be accessed with https://doi.org/10.5285/8933AF23-E051-4166-B63E-2155330A21D8. Reaction-Transport Model code (Si BRNS) can be accessed with https://doi.org/10.5281/zenodo.6023767.

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