

## Author Response to Comment on bg-2022-51

Author Response to Anonymous Referee #2

Author Response to Referee comment on "Benthic Silicon Cycling in the Arctic Barents Sea: a Reaction- Transport Model Study" by James P. J. Ward et al., Biogeosciences Discuss., <https://doi.org/10.5194/bg-2022-51-RC2>, 2022

The manuscript by Ward et al. use previously published geochemical data (dissolved Si,  $\delta^{30}\text{Si}$ ; Ward et al. 2022) of sediment pore waters and solid phases from 3 stations in the Barents Sea in an attempt to better understand the reaction pathways controlling the cycling of Si at the seafloor, (e.g. the dissolution of LSi and bSi, coupling of Fe and Si cycles, and the potential precipitation of AuSi). They employ a reaction-transport model (steady state and transient) to try and understand the pathways controlling the biogeochemical cycling of Si. The paper is mostly very well written, with some very interesting hypotheses (e.g. the possibility of being able to detect authigenic silica as a sink of silicon). However, the logic of the paper can be sometimes be difficult to follow, from the reader's perspective. There are some sections that are a bit confusing, and I have tried to provide some constructive feedback on the order of presenting the information (see below). My review includes a mixture of minor and major comments following the order of the text and sections of the manuscript.

***We thank the reviewer for their constructive comments and are happy to address the issues raised.***

**Line 16 to 17**– What do you mean by the phrase “taken-up” in this sentence? Are you suggesting that 2.9-37% of the released DSi has a value of -2 ‰?

***Thank you for your comment. We have reworded this sentence for clarity. In the best-fit model simulations, 3-37% of the DSi released from BSi and LSi dissolution is subsequently removed from the solid phase by a process that has a fractionation factor of  $\sim -2$ ‰, most likely representing authigenic clay mineral precipitation (lines 16-18).***

**Lines 144**– The assumed value of 50 mm for  $\text{AuSi}_{\text{sol}}$  is not from Ward et al. it comes from Lermann et al. 1975, I believe.

***Thank you for highlighting this. Line 143 has been amended accordingly (please see the attached highlighted manuscript).***

**Figure 2.** It would be useful if the authors could indicate that the steady state model simulations were from what is proposed in this paper.

***Thank you for your suggestion. We have amended the Fig. 2 caption to specify that the steady state simulations that contributed to the schematic are specifically from this study.***

### **Section 2.1.4 – Transient reaction-transport modelling**

I had a hard time following this section. Would it be possible to include a table or figure that could help the reader to understand the values associated with the input and outputs for this part of the model? For example, **lines 219 to 223** – present an additional, more reactive BSi phase – but no data is provided. What does this look like in numbers?

*Thank you for your suggestion. We have rephrased the description on Lines 219-221 for clarity. The bloom-derived BSi is not an additional/new phase *per se*, instead this more reactive phase was modelled as a temporary increase in the deposition flux and reactivity of the BSi phase already incorporated in the reaction network. We hope that the further description of the transient boundary conditions (i.e. deposition flux, BSi reactivity and bloom timeframe) in the following paragraph is sufficient, alongside Fig. 4, in demonstrating what the bloom-derived BSi flux looks like in numbers across the bloom period and in describing how it is modelled.*

Also, it is mentioned **on line 225** that the conditions are either 1 or 3 weeks but that the deposition flux was -8 to 26-fold whereas in the figure 4, which is presented in the text before figure 3, The fluxes appear to be 10, 20, 30 and 26-fold.

*Thank you for highlighting this error. The text on line 226 has been amended (a 10 to 30-fold increase).*

Also, it is not clear why the figure presents 3 sub-figures (bloom, 1.5 months, 3 months) based on the detail provided in section 2.1.4. I had to read section 3.2 at the same times section 2.14. Please add more information to these sections and to the title for Figure 3.

*Thank you for your suggestion. In addition to the description in section 3.2 (lines 432-444), we have also included a brief description on lines 236-239 for readability of section 2.1.4. We have also expanded the Fig. 4 caption to further describe the three panels.*

## **Section 2.2**

**Lines 249 to 260** appear to be disconnected from this section. It should be removed and/or perhaps placed in the discussion section.

*Thank you for your suggestion. This paragraph has been moved to section 3.1 as an introductory paragraph to the model results/discussion section (lines 276-293).*

Also, I wasn't aware that a fractionation factor of AuSi formation had been established nor that most people assumed that silicon isotope fractionation did not occur during dissolution. These are rather controversial points that should be presented more carefully.

*Thank you for your suggestion. We have rephrased this section to reflect that a fractionation factor for authigenic clay precipitation has not yet been established, and that the fractionation factors referred to in this paragraph are from studies of riverine and terrestrial environments (lines 276-289). We have also made our description of isotopic fractionation during BSi/LSi dissolution clearer (lines 289-294), by emphasising our point that some studies have shown that BSi dissolution occurs without fractionation, while others have demonstrated a slight enrichment of the lighter isotope in the dissolved phase. Consistent with previous reaction-transport model studies of the benthic Si cycle (Ehlert et al., 2016; Geilert et al., 2020), here we assume no fractionation during the dissolution of BSi/LSi.*

## **Results and Discussion**

The authors provide a great deal of information in this section and it would be useful to have an introductory paragraph before section 3.1 to give a brief outline of what is to be expected as points of discussion. It is quite easy to get lost in the details provided. For example, an introductory paragraph could summarize the principle hypotheses that are to be discussed.

**Thank you for your suggestion. We have provided a short introduction for section 3 (lines 264-273), which summarises the goals/aims outlined initially on lines 48-75. We have also moved the section that discusses which early diagenetic reactions fractionate Si isotopes to section 3.1 (originally on lines 249-260).**

Along these lines, I am not quite sure why the authors did not choose to present the transient dynamics by phytoplankton blooms in section 3.1. I understand that this is not at steady-state, but it might be worthwhile to mention the possibility that the system is not at steady state. For example, on **lines 334-337**, the authors talk about dissolution dynamics and the lack of BSi in the Barents Sea. They could mention, in this section, that it is possible that the reaction-transport model is limited since it only operates under steady-state conditions, and then mention that they will discuss this further in section **3.2**.

**Thank you for your suggestion. We have added a brief discussion on lines 331-334 to highlight that the steady state model is limited as it cannot resolve all the dynamics at station B14 (e.g. the pore water DSi concentration profiles for 2017 and 2019). Evidence has not been found for transient dynamics at stations B13 and B15, and the isotopic composition and DSi concentration data can be reproduced by a model that assumes steady state. The authors therefore believe that B13 and B15 are at steady state, but could well be influenced by transient dynamics throughout the year that were not sampled due to a rapid recovery/return to steady state conditions. The authors have decided to separate the transient model discussion into its own section because of the lack of evidence for non-steady state dynamics at stations B13 and B15.**

Again, along these lines, it might be worthwhile to include in the title of section 3.2 that this still implies the use of the reaction-transport model...

**Thank you for your suggestion. We have amended the title of section 3.2 to refer to transient reaction-transport modelling.**

Regarding sections 3.1 and 3.2, I remain unconvinced by some of the arguments presented by the authors that the isotopically heavier signal (from 0.5 to 2.5 cm) is solely coming from LSi. I am not saying that it is not a plausible argument, but I wonder why the authors did not propose that benthic diatom activity could also be an explanation. Benthic diatoms have been found (alive) at incredible depths in the Barents Sea (Druzhkova et al. 2018), and they may be causing this observed shift in the top few cm of the sediment. At the very least it should be mentioned why this was not considered as a possibility. For example, the authors could make an argument after conducting a mass-balance calculation to show whether it is (or is not) possible.

**Thank you for your suggestion. Druzhkova et al. 2018 observed three species of autochthonous benthic diatoms at up to 245 m water depth in the central Barents Sea, with cell counts of 67-365 cells/cm<sup>2</sup>. Previously reported DSi quotas per diatom cell typically range from 0.01-1 pmol/cell (Li et al., 2016-[doi.org/10.5194/bg-13-6247-2016](https://doi.org/10.5194/bg-13-6247-2016); Olsen and Paasche, 1986-[doi.org/10.1080/00071618600650211](https://doi.org/10.1080/00071618600650211); Lomas et al., 2019-[doi.org/10.3389/fmars.2019.00286](https://doi.org/10.3389/fmars.2019.00286)). For the following mass balance calculation, we assume the maximum cell quota (1 pmol/cell) and cell count (Druzhkova et al. 2018), as well as an 8  $\mu$ M average core top water DSi concentration for a theoretical area of 1 m<sup>2</sup> and 2 cm deep (0.02 m<sup>3</sup>) at the sediment-water/core top interface.**

The aforementioned values give a DSi stock in the theoretical volume of 160  $\mu\text{mol}$  DSi and a maximum of 3.7  $\mu\text{mol}$  DSi stored in the diatoms across that theoretical space. Modelling this system (at station B14 for example) under a steady state scenario (see equations in Grasse et al., (2021)-[doi.org/10.3389/fmars.2021.697400](https://doi.org/10.3389/fmars.2021.697400)), assuming an average fractionation factor during DSi uptake by diatoms of  $-1.1\text{‰}$  (De La Roach et al., 1997; Sutton et al., 2013) and an initial  $\delta^{30}\text{Si}$  of  $1.17\text{‰}$  (equivalent to the average 0.5 cm pore water composition across the three cruise years), gives a predicted  $\delta^{30}\text{Si}$  of  $1.19\text{‰}$ , which is much lower than the measured average isotopic composition at the 1.5-2.5 cm peak ( $1.48\text{‰}$ ) (maximum  $f = (160 \mu\text{M} - 3.5 \mu\text{M})/160 \mu\text{M} = 0.98$ ). A Rayleigh fractionation scenario also gives a predicted  $\delta^{30}\text{Si}$  at the pore water peak of  $1.19\text{‰}$ , under the same boundary conditions.

These calculations indicate that the autochthonous benthic diatoms are not present in a high enough abundance to be solely responsible for the shift towards heavier isotopic compositions downcore from 0.5 cm to  $\sim 2.5$  cm sediment depth. This observation is consistent with our previous findings, which show that Barents Sea surface sediments are characterised by low BSi contents (0.26-0.52 wt%). Furthermore, the depth of the stations studied here range from 295-359 m, which is greater than the depth at which the autochthonous benthic diatoms were found, suggesting they may exhibit an even lower abundance at stations B13, B14 and B15.

We have added lines 327-330 to the main text to acknowledge the presence of benthic diatoms in the Barents Sea, that are likely to be taking up DSi, but that they are not in a high enough abundance to influence the isotopic composition of the sediment pore water DSi pool to a significant degree. These observations, in addition to the evidence presented in Ward et al., GCA (in press), support the precipitation of authigenic clay (AuSi) as the driver of the downcore increase in pore water  $\delta^{30}\text{Si}$  between 0.5 cm and 2.5 cm depth across the three stations.

Ideally, it seems as though it would be helpful to conduct empirical assessments (batch or open conditions) of the dissolution of sediments to test whether the hypotheses are plausible for the dissolution of LSi, BSi, and the links between the Fe and Si cycles over time. Since very little work has been done really evaluating these aspects, it would be very useful for the authors to suggest the need for more empirical studies in order to support (or not) the model results from this work.

**Thank you for your suggestion. We have expanded our recommendations for future work at the end of section 3.5 by including batch and/or flow-through experiments to investigate dissolution (BSi/LSi) and precipitation (AuSi) dynamics, as well as the coupling of the Fe and Si cycles (lines 631-633).**

**Figure 3.** I do not see the interest in showing a model of the BSi content, in particular since it is based on only 3 data points per station.

**Thank you for your comment. The BSi content was a key parameter for the fitting of our observational data, used to constrain the boundary conditions for the dissolution of BSi as opposed to assuming published values for the reactivity or exponential attenuation function. The authors have therefore decided not to remove the BSi content panel in Fig. 3.**

**Lines-434 to 435:** why does your simulation data ( $k_{\text{dissbloom}}$ ) have higher values than the published data, even higher than the dissolution rate constant of diatom at warm temperature (14-22 degrees)? The reactivity of fresh diatoms varies due to

temperature: high reactivity of diatoms has been observed at a higher water temperature region, whereas low reactivity of diatom material was observed in cold water, and the differences can be more than 10-fold (Ragueneau et al., 2000). Therefore, the reactivity of diatom bSi in your modeling of the Arctic area (<2 degrees) might be much lower than what was used in the model.

**Thank you for highlighting this. We have amended lines 460-466 to acknowledge the sensitivity of BSi reactivity/dissolution rate constants to in-situ temperature and species composition. The reactivity of fresh diatoms is thought to range from ~3-100 yr<sup>-1</sup> (Ragueneau et al. 2000; Nelson and Brzezinski, 1997), although Roubex et al., (2008) suggest that at 18-23 °C, dissolution rate constants range from 1.5 to 150 yr<sup>-1</sup> across different diatom species. Our modelled scenarios cover a range of 5-20 yr<sup>-1</sup>, which is also within range of the reactivity of fresh/cleaned diatoms measured at much lower temperatures in seawater (27 yr<sup>-1</sup> at 2°C (Rickert, 2000) and 6 to 131 yr<sup>-1</sup> at 4°C in Kamatani and Riley, (1979) depending on the stage of dissolution).**

**The authors recognise that BSi reactivity can decrease with a reduction in temperature (e.g. 4 to 14-fold lower at -2 vs 12 °C (Tréguer et al., 1989-[doi.org/10.1007/BF00442531](https://doi.org/10.1007/BF00442531))), as well as across different species. The water column BSi dissolution temperature coefficient (Q<sub>10</sub>) is ~2.3 - 2.9 (Kamatani, 1982- [doi.org/10.1007/BF00393146](https://doi.org/10.1007/BF00393146) ; Bidle et al., 2002-[doi.org/10.1126/science.1076076](https://doi.org/10.1126/science.1076076) ; Natori et al. 2006-[doi.org/10.1016/j.marchem.2006.04.007](https://doi.org/10.1016/j.marchem.2006.04.007)), thus the BSi dissolution rate at 0 °C would theoretically be 5 to 8.4-fold lower than the rate at 20 °C. However, previous experiments have shown that dissolution rate constants much greater than those needed to resolve the transient/non-steady state dynamics at station B14 have been observed at low temperatures. We suggest that the physical mixing dynamics at the polar front (station B14) are able to efficiently deliver fresh, reactive BSi to the relatively shallow Barents Sea seafloor (as it has been shown to do for organic carbon (Wassmann and Olli, 2004)), which rapidly dissolves and drives stark transient peaks in pore water DSI concentrations of the uppermost sediment layers.**

**Line-457:** study carried out by Moriceau et al., 2009 reported at least 2 types of bSi, this reference may also be relevant to your study.

**Thank you for your suggestion. We have included this reference and amended the text on lines 489-492.**

**Line 525:** please use the updated values for burial efficiency provided by Tréguer et al. (2021)

**Thank you for your suggestion. We have adapted lines 553-564, to reflect the updated burial efficiency from Tréguer et al., (2021). The burial flux magnitude is 46% higher in the 2021 review than the 2013 review, but the burial efficiency is similar: 3.6% vs 3% of the global marine gross BSi production. Here we report burial efficiency values as a proportion of the BSi deposited at the seafloor (11% calculated from Fig. 1 in Tréguer et al., (2021) and calculated in Frings (2017) ([doi.org/10.1007/s11631-017-0183-1](https://doi.org/10.1007/s11631-017-0183-1))). Barents Sea stations therefore exhibit similar burial efficiencies to the global average, but lower than most values that are reported for continental shelf sediments.**