Author Response to Comment on bg-2022-51

Author Response to Anonymous Referee #1

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-RC1, 2022

The manuscript by Ward et al. reports on the benthic-pelagic coupling in the Barents Sea with special emphasis on the Si cycle. The authors identified and described the biogeochemical reactions using silicic acid concentrations and Si isotopes and evaluated the reactions by reaction-transport modelling. The authors identified the dissolution of biogenic and lithogenic silica and silicon attached to dissolving iron phases as the major Si sources and authigenic clay precipitation as major sink. Also, the rapid dynamics and adjustment of the reactivity of the different sedimentary phases with respect to changing BSi supply and blooms are discussed and highlighted. Finally, the importance of benthic Si cycling for the Arctic Ocean Si budget is emphasized.

The manuscript is very well written and nicely discusses the main findings of this study. However, during reading the manuscript, I felt an increasing frustration with the many references to the other manuscript of Ward et al., which is currently under review in GCA. I appreciate that the authors provided a link to the preprint, but given that the method section (especially the sequential extraction and Si isotope measurements) and some parts of the interpretation and hypothesises are still under review leaves me with some concerns. In general, I am highly confident that the applied methods are correct and tested thoroughly, but I would only support a publication of this manuscript after the full review process and acceptance of the related GCA-manuscript. Apart from that, I am recommending this manuscript for publication with moderate revisions (see below).

We thank the reviewer for their constructive comments and are happy to address the issues raised. The GCA manuscript has now been accepted for publication (doi.org/10.1016/j.gca.2022.05.005), which includes all the Si isotope measurements. The sequential sediment digestion protocol was published in Pickering et al., (2020) (doi.org/10.1029/2020GL087877).

Introduction: I would start with a general introduction of the importance of the benthic silicon cycling as you have done in lines 69-78.

Thank you for your suggestion. We have restructured the introduction to begin with the importance of the Si cycle and have moved some of the wider context into an oceanographic context section within the methods (lines 78-104).

I guess, a reference to Fig. 2 is missing in the introduction! It is mentioned first time in line 449.

Thank you for your comment. Fig. 2 is referred to on line 109 and we have added an additional reference on line 99 (please see the attached highlighted manuscript).

Fig. 2: It is not clear at this point of the manuscript whether the reactions described in the red box are assumptions or data interpretation. Only later on in the text it becomes clear that these are modelling results.

Thank you for highlighting this. We have specified in the Fig. 2 caption that the red box schematic is derived from the results of the simulations carried out in this study.

Line 144: Instead of Ward et al., I would cite here the references you mention in the Table S2 (Lermann et al., 1975; Hurd, 1973).

Thank you for your comment, the references on line 143 have been amended accordingly.

Line 333-337: In this study, you discovered that some assumptions you made in your other study, which is also still under review, are not valid anymore. I would strongly recommend to use the possibility of changing the interpretation in your GCA manuscript, if you already know it is incorrect (concerning the AuSi precipitation in the upper 0.5cm)!

Thank you for your comment. Without introducing the model into the observational data paper, it was not possible to introduce the alternative estimate for the contribution of LSi to the DSi pool. The model simulations build on and complement the observational data, but it was outside the scope of our GCA paper to incorporate the model results. Further, we have made multiple assumptions/simplifications in the model regarding LSi dissolution dynamics, as discussed in the text. Therefore, both the model and observational data-derived estimates provide two values for the contribution of LSi to the sediment pore water DSi pool, based on different methodologies, however both incorporate certain limitations/assumptions.

Line 183: definition missing for RMSE

Thank you for highlighting this, we have now included a definition for RMSE on line 182.

Line: 250ff: for marine systems, no fractionation factor of authigenic clay formation is yet thoroughly established. The phrasing like it is sounds misleading. The studies you are referring to are either land-based, riverine or experimental. I agree that the size of the fractionation factor is likely correct, however, I would formulate this more carefully. Ehlert et al. (2016, GCA) modelled a fractionation factor of -2‰ for marine authigenic clay formation, which was also found in Geilert et al. (2020, Biogeosciences), but it can reach up to -3‰ in deep-sea settings (Geilert et al., 2020, Nat. Comm.), likely depending on pore water properties (pH, temperature, salinity, saturation states). This high fractionation factor would also agree with the repetitive number of dissolution-reprecipitation cycles discussed in Opfergelt & Delmelle (2012).

Thank you for your suggestion. We have rephrased this section to reflect that the fractionation factors referred to are established for clay formation in riverine and terrestrial environments, rather than authigenic clay precipitation specifically (lines 276-293).

Lines 275-340: it would significantly help, if you would refer to the model lines (colour, dashed, ...) shown in Fig. 3, when discussing the data. Like this, it is really difficult to connect the text with the various model results. Please also indicate in the legend in Fig. 3, what conditions cause the 'best fit'.

Thank you for your suggestion, we have now referred to the plot line colours throughout sections 3.1.1 and 3.1.2 (dashed blue/red and solid grey/black) to improve readability. We have also specified in the caption of Fig. 3 that the best

fits require the dissolution of BSi and LSi, as well as AuSi precipitation and Si desorption from Fe (oxyhydr)oxides, and to refer to Table S2 for a full description of the boundary conditions imposed for the best fit simulations.

Line 321: Considering the solubility of clays, can they really dissolve here? The dissolution rates of clays are much lower in seawater compared to primary minerals like feldspars or basaltic glass (see e.g. Jeandel & Oelkers, 2015).

Thank you for highlighting this point. The authors acknowledge that the rate of dissolution for primary silicate LSi phases will be higher than for secondary phases. However, multiple experiments have demonstrated that clay minerals can rapidly release silica into DSi-depleted seawater (0.3-5 μM- not dissimilar to core top waters in this study (4-10 μM)) (some experiments were carried out at low temperatures of 1-2°C, most at room temperature. See Table S3), as well as take up DSi in DSi 'enriched' seawater (17-416 μM). Generally, these experiments show that a DSi concentration plateau is approached within four to 500 days (Fanning and Schink, 1969; Mackenzie et al., 1967; Lerman et al., 1975; Mackenzie and Garrels, 1965; Hurd et al., 1979), similar to asymptotic and pseudo-asymptotic concentrations in this study (~100 μM). Mackenzie and Garrels (1965) show a plateau after six months for six clay minerals, but note that >50% of the DSi contributing to the apparent solubilities was generally released within the first 10 days. Further, Köhler et al., (2003) (where the dissolution rates are taken for illite in Jeandel & Oelkers (2015)) show that at a low initial DSi concentration (5 μM) at 5°C, DSi concentrations reach 140 μM after just 140 days (although the solution was not seawater).

We also thank the reviewer for the link to Jeandel & Oelkers (2015), who suggest that clay minerals dissolve at a rate equivalent to ~0.1% of the clay (kaolinite and illite) mineral pool per year. Given the low rates of sedimentation estimated for the Barents Sea (average 0.07 cm/yr) (Zaborska et al., 2008), the length of the sediment cores (35 cm) represents ~500 years, corresponding to roughly half of all the clay material deposited at the sediment-water interface. Therefore, while the rate of dissolution is much lower than for primary minerals (e.g. apatite, labradorite, basaltic glass), over half of the material could theoretically dissolve across the sediment core lengths studied here. 96% of all the material at the sediment-water interface is estimated to constitute detrital material (Ward et al., GCA in press), therefore this would indicate over half of all the material could dissolve by the base of the core even at the lower rates of mineral dissolution.

In addition to the experimental settings discussed above, previous studies have inferred the dissolution of clay minerals in marine sediments (e.g. Geilert et al., 2020; Vorhies and Gaines, 2009; Abbott et al., 2019- doi.org/10.3389/fmars.2019.00504), and while clay minerals are typically considered a relatively stable end-product of weathering, fine clay particulates and reactive surface sites (e.g. montmorillonite, smectite, and illite) have been shown to dissolve in natural waters (Geilert et al., (2020) and references therein).

We have included a caveat on lines 350-351 to reflect that, while the δ^{30}Si measured in the Si-NaOH pool (LSi) (-0.89‰, Ward et al., GCA (in press)) is within range of clay minerals (-2.95 to -0.16‰), rather than primary silicates (0 to -0.34‰), this value could also represent a combination of the two, thus potentially representing dissolution of reactive primary phases as well as clays (e.g. labradorite, basaltic glass or forsterite that dissolve at a rate of 20-40% per year (Jeandel & Oelkers, 2015)).

Would it be possible that during your sequential leaching procedure you dissolved some of the authigenic clays here as well, shifting the bulk LSi phase δ^{30}Si to lower values?

The reactive Si pools studied here are operationally-defined (Pickering et al., 2020) and so it cannot be completely ruled out that some authigenic clay minerals have dissolved within the 4 M NaOH digestion, as there is inevitably some overlap across the pools. However, the 0.1 M HCl treatment is thought to remove authigenic products that coat BSi (e.g. Fe (oxyhydr)oxides and authigenic clays) (Pickering et al., 2020) and the mild alkaline (0.1 M Na_2CO_3) digestion activates the BSi phase as well as some LSi, which can then be corrected following Kamatani and Oku (2000) (Ward et al., GCA in press). Further, Michalopolous and Aller (2004) showed that mild acid leaches (0.1 M) dissolve authigenic clay coatings on BSi and note that poorly crystalline authigenic clays can also dissolve in distilled water within 24 hours (see references therein). The authors would therefore expect that the previous two digestions would have removed the highly reactive authigenic clays before the harsher alkaline digestion with 4 M NaOH.

Lines 389-395: I wonder, if the model simulation gives a dissolving phase of -1 to -1.5‰, why not consider a higher contribution of lithogenic silica in this depth, which is much closer to the modelled value (about -0.9‰) than the FeSi phase (-about 2.9‰)? Do you really need a FeSi phase here to reproduce the pore water variability? I also wonder, if it is mass balance wise feasible? How much Si needs to be attached to this Fe-phase to create such a distinct peak in pore fluid δ^{30}Si? And why is it then not seen in DSi?

Thank you for your comment. In most sediment cores studied here, pore water DSi concentrations approach 80-100 μM at the depths where we see shifts towards lighter isotopic compositions at all three stations (Fig. 3). 80-100 μM equates to or surpasses the solubility of many primary and secondary silicate minerals in seawater at low temperatures (Table S3). Although, we recognise that some primary silicates in particular (e.g. olivine and some pyroxenes) can exhibit solubilities far greater than this (175-300 μM) (Hurd, 1979). The authors believe it is likely that the rate of LSi dissolution will slow considerably as Barents Sea sediment pore DSi concentrations approach equilibrium of many silicates (Lerman et al., 1975), especially given that Barents Sea sediments are clay-rich and so will likely lack considerable amounts of fresh primary silicates that would increase the average solubility of the bulk sediment.

Furthermore, in order for LSi dissolution to be the cause of the shift towards lighter Si isotopic compositions at specific depths at all three stations, a mechanism would be needed to explain a sudden increase in the rate of LSi dissolution within a particular sediment horizon. Given that the depths where we observe shifts towards lighter isotopic compositions also correspond to the shift to hypoxic/anoxic conditions (indicated by O_2 and NO_3^- concentration data (Ward et al., GCA in press)) and corresponding increases in dissolved Fe concentrations, the authors believe the most likely driver is the reductive dissolution of Fe (oxyhydr)oxides.

If we assume an FeSi Si isotopic composition of -2.89‰, approximately 12-25% of the DSi in the sediment pore waters below the redox boundaries (where we observe the isotopic shifts) is composed of DSi derived from FeSi. 12-25% corresponds to 11-26 μM, which is not observed in the DSi concentration profiles, likely due to uptake during the precipitation of AuSi. Authigenic clay formation is thought to occur throughout the core lengths, as indicated by cation concentration profiles (Ward et al., GCA in press), although

this process is likely enhanced near the sediment-water interface. This hypothesis is consistent with the simulations in this study, which require low levels of AuSi precipitation to continue at depth in order to generate best fits of the DSi concentration and isotope profiles (parameter 'ap' in Table S2). Providing the composition of the dissolving phase is isotopically light enough (e.g. -2.89‰) to offset the uptake of excess DSi through AuSi precipitation, this could explain why the process is seen in the isotope signals and not the DSi concentration profiles.

Section 3.2: Also here it would be easier to follow your arguments if you would refer to the colour coding of the model results in Fig. 4.

Thank you for your suggestion, we have now referred to the line colours throughout sections 3.1.1 and 3.1.2 (dashed blue/red and solid grey/black) to improve readability.

Figure 4: Why are the different scenarios in 'bloom initiated' only modelled for the x30, 15ye-1, 1wk scenario? Why not for the different multipliers, duration? Do you assume the bloom lasted only for one week as mentioned in line 426? In this case, I would add a comment in the caption as well.

Thank you for highlighting this. All the bloom scenarios were run in the 'bloom initiated' panel, however because this panel represents a very early timestep of the simulation, the model results are equivalent to the steady state simulations. The subsequent panels ('+1.5 months' and '+3 months') demonstrate the effect of the increased BSi deposition over time. We have now specified in the Fig. 4 caption that the 'bloom initiated' panel effectively represents time = 0 and so the different simulation results overlap. We have also specified in the caption that '+1.5 months' and '+3 months' refer to the time elapsed since the bloom was initiated for clarity.

Line 417: Which 'certain conditions' do you mean here?

Thank you for your comment. We have removed the phrase 'certain conditions' and referred to Fig. 4 instead (lines 444-445). This makes it clearer that the bloom-derived BSi can drive peaks in pore water DSi concentrations, depending on reactivity, rate of deposition and length of bloom (as described on line 234), which is not to be confused with the wider boundary conditions in Table S2.

Line 426: This combination of parameters does not exist in the legend in Fig. 4

Thank you for highlighting this error. We have changed the value to a 30-fold increase on line 453 (30X flux , 15 yr^{-1} $k_{dissbloom}$, 1 wk).

Line 525: The total ocean average BSi burial efficiency was revised in Tréguer et al., 2021 (Biogeosciences). The authors found a much higher burial efficiency compared to the findings of Tréguer & De La Rocha, 2013. How is that higher burial efficiency impacting your data interpretation?

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)). Barents Sea stations therefore exhibit similar burial efficiencies to the global average, but are lower than most values reported for continental shelf sediments.