

We thank Reviewer #3 for their time in reviewing our manuscript and the comments they have raised, particularly concerning the method of analysis, which have contributed to improving our work. Here we include responses to all of the comments as follows: (1) Reviewer's comment (2) Author's comment (3) Suggested change to the manuscript.

(1) Method part, L145-L148: I understand that it is difficult to measure  $\delta^{30}\text{Si}$  of samples with low DSi concentrations. However, it is not common nowadays to report  $\delta^{30}\text{Si}$  values based on the measurements of  $\delta^{29}\text{Si}$ . This practice will be more justified if the authors could provide more details (can be in the supplementary) on why it was not possible to measure  $\delta^{30}\text{Si}$  directly. For example, what kind of efforts the authors have already put into trying to resolve the matrix effects and interferences? Normally anion doping (sulfate, nitrate, etc...) or pre-removal of organic matter could help to diminish the matrix effect (Closset et al., 2016; Hughes et al., 2011). Isobaric interferences of e.g., nitrogen ( $^{14}\text{N}_2$ ) and nitric oxide ( $^{14}\text{N}^{16}\text{O}$ ) can be avoided by medium resolution mode focusing on the left side of the peak shoulder (Liguori et al., 2020). At least it would be nice to see that the authors have already tried all these approaches before giving up on directly measuring  $\delta^{30}\text{Si}$ .

(2) We thank reviewers #1 and #3 for their comments on measuring d29Si and for giving us the opportunity to elaborate on the methods of measurements, as we realise the writing of the method section reads as if the d30Si isotope of samples was not measured. To clarify, all three isotopes were measured during analysis and a strong relationship was found between measured d29Si and d30Si ( $d29\text{Si} = 0.5131 \cdot d30\text{Si}$ ,  $R^2 = 0.99$ ), but larger variability and standard deviations were measured on the d30Si. The left side of the peak shoulder was measured for each measurement in medium resolution as it is the standard practice of analysis for Nu plasma II MC-ICP-MS. An increasing number of laboratories has been reporting  $\delta^{30}\text{Si}$  values based on the measurements of  $\delta^{29}\text{Si}$  for the comparison of datasets, particularly at very low DSi concentrations (most recently for the Arctic Ocean: Liguori et al., 2021). Considering the robust relationship measured between d29Si and d30Si in our dataset, we found the method of conversion preferable to anion doping which we experienced within the wider context of this project and found to slightly increase variability in our measurements. (3) The method description has now been amended for clarity on our method of analysis and we will include a supplementary material section illustrating the d29Si vs d30Si of our measurements.

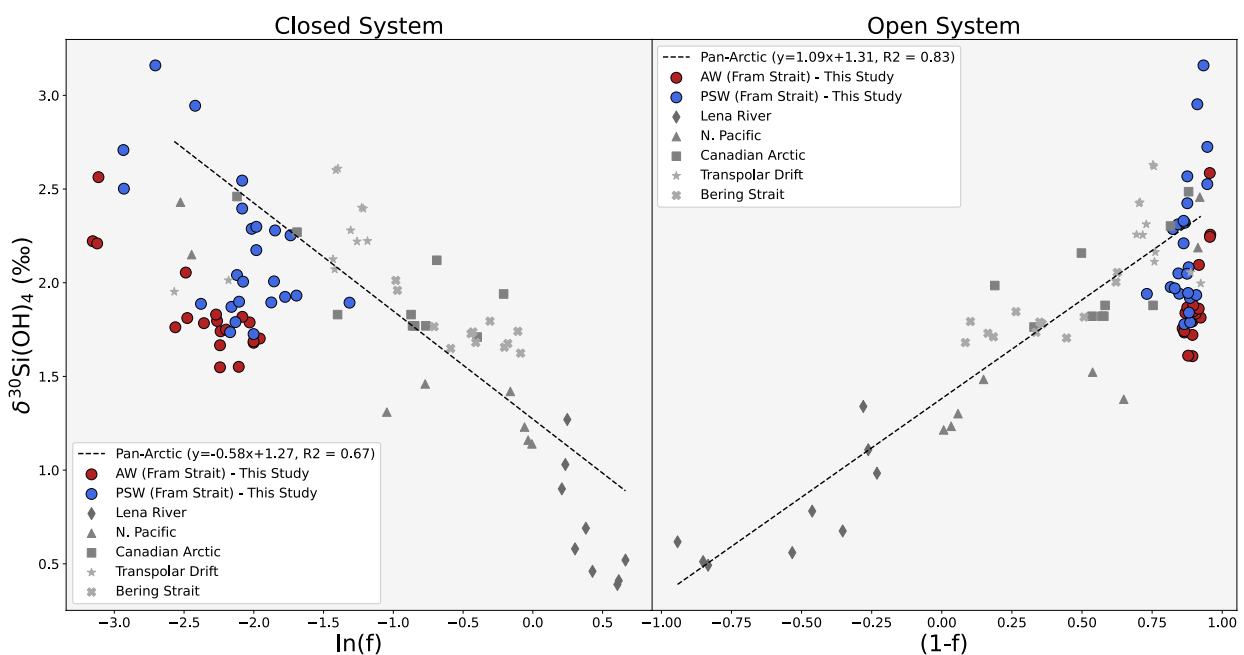
(1) The initial level of the nutrients before utilization should be the subsurface water from the time period with strong mixing prior to the sampling, i.e. winter season. Initial condition for both spring and summer seasons should be the same (i.e. upwelled winter subsurface water). The authors did not give too much details of their choice on the initial condition, but it seems like they simply chose the subsurface waters in each sampling event as the initial condition. On the other hand, considering the horizontal transport of the water mass (i.e. PSW and AW), the initial condition might be found horizontally. Therefore, I wonder whether the authors' choice of the initial condition of the model is correct and I recommend the authors to provide more information on this aspect. 2) It makes more sense to separate PSW and AW dataset into different models because their initial conditions are different. Spring and summer dataset from the same water mass should be combined into the same model, because they belong to the same fractionation system, i.e. the nutrient kept being

utilized in summer after the utilization in spring. 3) In figure 6,  $\delta^{30}\text{Si}$  data do not fit any of the models during any of the sampling events, so the discussion between L257 to L260 is not valid. This might point to the incorrect choice of initial condition that the authors applied to calculate the nutrient utilization.

(2) We thank Reviewer #3 for their comment on the initial conditions of the Rayleigh fractionation model and general suggestions as we believe this has contributed to improve our manuscript. Following suggestions from all reviewers, we have updated the parameters of our Rayleigh model in Figure 6, improving the fit of the  $\delta^{30}\text{Si}$  data. (3) Panels are now separated by watermasses rather than by season. Initial conditions were chosen from subsurface waters and we discuss the importance of horizontal transport within the manuscript. (2) Adjustments made to the Rayleigh model is addressed in more details in the general comment to all reviewers.

(1) It is not justified to estimate the PSW Si:N (that free of terrestrial influence) based on the assumption of “further modification of marine  $\delta^{30}\text{Si}(\text{OH})_4$  and DSi:N through the Bering Strait is linear with North Pacific trends”. Especially after the authors already concluded that nitrate was largely removed via denitrification in the Arctic, which will clearly modify the Si:N within the Arctic. It is thus not convincing to conclude DSi:N>0.78 in the PSW must originate from terrestrial riverine sources. Therefore, the estimation in the paragraph L434-441 is not valid.

(2) We have taken this comment onboard and have now independently evaluated the composition of PSW DSi using the estimated Arctic-wide fractionation factor from the robust pan-Arctic Rayleigh trend ( $R^2= 0.67$  &  $0.83$ ) shown in Figure 8 (now including data from Giesbrecht et al., 2022) & subsequent apparent utilisation of nutrients in PSW. Closed and open fractionation trends are shown in the two graphs below (included in supplementary material S4). Using this method, we calculate a pan-Arctic isotope effect  $30\epsilon$ ,



and calculate that around 50% of nutrients from shelf and halocline waters are utilised in PSW. From this updated calculation we find riverine sources contribute to  $40 \pm 4\%$  of the total DSi inventory at Fram Strait, with Pacific sources contribute to around  $8 \pm 1\%$ . We believe this new calculation to be more robust than the original evaluation based on Si:N ratio and (3) the discussion in the paragraph L434-441 has been updated accordingly.

(1) Additionally, as the authors illustrated the mixing scheme in Figure 10, it is quite obvious that Si:N of the PSW is located within the error of the mixing line between the AW and E.S. Shelf. This indicate that the increase of Si:N in the PSW is more a result of the shelf CPND. The only prominent outliers of PSW dataset beyond the mixing lines are the three data points with lower Si:N/heavier  $\delta^{15}\text{N}$ .

(2) As per our discussion in section 4.1.2, we agree that the dominant influence on  $d^{15}\text{N}$  is from shelf CPND, which will impact Si:N. Terrestrial influence is however observed on the Pan-Arctic trend, and to a smaller extent, within PSW, with lower  $d^{15}\text{N}$  and higher Si:N than expected from the linear regression. Although the PSW dataset fall within 1SD of the linear regression, a large part of the measurements fall below the mean where  $\text{DSi:N} > 1$ . This trend is further supported by separate measurements from the Eurasian shelves (Laptev Sea) and over the continental slope (Debyser, in preparation).

(1) L130-139: The two-step co-precipitation has been widely used previously, so there is no need to elaborate its necessity here. It can be directly cited from previous work, for example (Reynolds et al., 2006), (Grasse et al., 2013), (Liguori et al., 2020) etc... (3) Method has now been edited down.

(1) L137: What does “regrouped” mean? (2) This refers to the regrouping of the two separate precipitate during the two-step preconcentration.

(1) L152: Please note whether the uncertainties are 1SD or 2SD. (2) Uncertainties are 1SD. (3) This is now included in the text.

(1) L181: Please add “in the upper 400m”. (3) Added

(1) L185: Please add (Figure 3c). (3) Added

(1) L189: Please add (Figure 3b). (3) Added

(1) L193-195: Please tone down the argument here, as  $(5.42 \pm 0.70 \mu\text{M})$  and  $(6.65 \pm 1.67 \mu\text{M})$  are within error identical. (3) Sentence now edited to read “Below the mixed layer, DSi is low in AW ( $5.42 \pm 0.70 \mu\text{M}$ ) from DSi poor Atlantic waters of sub-tropical origins. DSi in PSW is slightly higher albeit within error of AW ( $6.65 \pm 1.67 \mu\text{M}$ ), potentially reflecting Arctic sources of DSi to PSW.”

(1) L196: Please add (Figure 3d). (3) Added

(1) Section 3.3: The description in this section is bouncing back and forth between figure 3 and figure 4&5, i.e. between whole depth profile and surface data. It will be clearer if the authors can give clearer information on which figure/panel the sentence refers to, and

describe the distribution from the surface to the deep for both Si and N/O isotopes. (3) References to panels and figures for each sentence of section 3.3 are now included.

(1) L234-235: "Nutrient utilization" is normally defined as the fraction of nutrient that has been utilized. The way that the authors define it here is against the common cognition. (3) Nutrient utilization changed to nutrient fraction (f) instead in the manuscript and figure captions.

(1) L291-293: The whole sentence "settling particulate nitrogen... sediment interface." reads a bit repetitive, please rephrase. (3) Sentence rephrased to read "[...] settling particulate organic nitrogen from coastal productivity degrades at the sediment interface of the extensive shallow shelves and produces large sources of sedimentary ammonium."

(1) Section 4.1.2 The authors try to discuss the modification of nitrate and DSi in the Arctic ocean in this section, so maybe the authors should exclude the dataset within the mixed layer, which are largely impacted by the local biological uptake. From Figure 7, only panel (c) excludes samples from within the mid-layer depth.

(2) We believe it is important to include datasets within the mixed layer in Figure 7.a, b and d as they illustrate how the variation in nutrients in both water masses lead to diverging trends within the surface layer, linking remote nutrient modification to biological trends at Fram Strait.

(1) L355: It is not easy to understand "merging towards signatures resembling riverine endmembers" here, please give the values of the riverine endmembers. (3) Values of riverine endmembers added to L355.

(1) L367: TDP → TPD. (3) Typo amended

(1) L372: The larger variability in Si isotope signatures of PSW ( $R^2 > 0.3$ ) at Fram strait might reflect the combination of mixing and local biological uptake. (2) We agree with this, (3) sentence has now been rephrased to read "[...] reflects the combined effects of local biological uptake and mixing between Arctic and Atlantic source signatures around Fram Strait."

(1) L376: valuated → evaluated. (3) Typo amended

(1) L397: while. (3) "While" removed from sentence.

(1) L409: ply? (3) Sentence rephrased to "[...] by mixing across the halocline in basins where AAW underlies below PSW" for clarity.

(1) Line 429-430: Please show the linear relationship between  $\delta^{30}\text{Si}$  and DSi:N in North Pacific waters. (2) Following our answer to comment 3 above, this is no longer relevant to

the discussion as estimations are no longer based on DSi:N and this has been removed from the discussion.

(1) L489: I would not describe a 0.11‰ increase of  $\delta^{30}\text{Si}(\text{OH})_4$  as “significantly” enriched, as the long-term reproducibility of the ALOHA<sub>1000m</sub> measurement is 0.08‰, the two values with a difference of 0.11‰ even overlap within error. (2) The enrichment we measure aligns with trends of enrichment measured across the Arctic (Varela et al., 2016, Brzezinski et al., 2021, Giesbrecht et al., 2022). We are confident that this is a trend within our dataset and not measurement error and have decided to keep the mention of this trend in our conclusions.

(1) Figure 2: the scale of temperature (left panel) is missing. (3) Figure is amended and temperature scale is now included.

(1) Figure 6: I wonder whether it is necessary to add the fractionation lines of the products, as there is no data from the biogenic phase and there’s no discussion of the fractionation of the products. Removing these unnecessary lines can make the plots cleaner. (3) Product fractionation lines have been removed from Figure 6, and biogenic phase measurements are now included in this work in the supplementary material S3.

(1) Figure 10: Please correct the sentence in the caption: “Dotted lines Solid line shows the regression (conservative mixing line) between AW and shelf endmembers endmembers, dotted lines are for one standard deviation.” Also, if the line is conservative mixing line, then it is not regression line. They are not the same. (2) The line displayed in Figure 10 is the regression line, not a conservative mixing line and (3) the caption has been edited to “Solid line shows the linear regression between AW and shelf endmembers, dotted lines are for one standard deviation”.

## References

Giesbrecht, K. E., Varela, D. E., Souza, G. F. and Maden, C.: Natural Variations in Dissolved Silicon Isotopes Across the Arctic Ocean From the Pacific to the Atlantic, *Global Biogeochem. Cycles*, 36(5), 1–23, doi:10.1029/2021gb007107, 2022.

Liguori, B. T. P., Ehlert, C., Nöthig, E. M., van Ooijen, J. C. and Pahnke, K.: The Transpolar Drift Influence on the Arctic Ocean Silicon Cycle, *J. Geophys. Res. Ocean.*, 126(11), doi:10.1029/2021JC017352, 2021.