

Response to review of *Silicon stable isotope distribution traces Southern Ocean export of Si to the eastern South Pacific thermocline* by G. F. de Souza et al. (Biogeosciences Disc.)

Reviewer #1: Damien Cardinal

We thank the reviewer for his careful and constructive review.

P6413, L1-2: *I really wonder why the authors used glass fiber filters to sample for silicon isotopes?...*

Yes, using glass fibre filters is clearly not ideal when sampling for Si. We shipped polyethersulfone filters for filtering our samples, but these unfortunately had too low a throughflow to allow inline sampling from the rosette, such that the sampling crew was forced to use GF/F filters from the CDOM sampling team instead.

The reviewer correctly points out that we should address potential contamination issues. We have filtered ultrapure water and low-Si (0.65–0.9 μM) seawaters through GF/F filters in the laboratory, and observed a 0.35–0.45 μM contamination after filtration of $\sim 20\text{ml}$ solution. Whilst such a contribution is completely negligible for almost all of our samples with high Si, this observation indicates that for the 8 near-surface, low-[Si] samples (i.e. $< 7 \mu\text{M}$), there might be a considerable Si contribution from sampling blank. With such a low absolute blank contribution, we cannot analyse its isotopic composition. Thus, it is not possible to accurately assess the influence of the blank on the measured $\delta^{30}\text{Si}$ values, which is an unsatisfactory situation. Nonetheless, we continue to have good confidence in the accuracy of our data from the low-Si samples: the samples that should be most vulnerable to contamination are the low-Si, high- $\delta^{30}\text{Si}$ samples of the surface Southern Ocean (considering that a glass contamination would be expected to have a low $\delta^{30}\text{Si}$ value around 0‰). As Fig. S4 shows, these samples are in good agreement with the published literature, which indicates (but cannot prove) that the influence of the sampling blank is not excessive.

Since we are unable to conclusively rule out the possibility of this contamination on the values we report for the 8 low-Si samples, we now explicitly alert the reader to the existence of this problem in the main text (Section 2, penultimate paragraph), highlight these samples in the data table and state conservative bounds within which we cannot rule out that the near-surface data is affected. Our estimation of these bounds is explained in a more detailed discussion of blank influence in the new Supplement A. Note that our discussion focuses on samples in the winter mixed-layer and deeper, which are all insignificantly affected by the filtration blank.

P6413, L20-25. *...for seawater samples replicated with 2-5 analyses, SEM provides an underestimation of the uncertainty.*

Agreed. We now provide 2SD errors for our data in the table and the figures.

P6413, L20-22: *Specify whether n analyses represent n replications of whole sample processing or rather n analyses of the same purified sample.*

These are complete replicates, as we state in the paper; i.e. at least replicated chromatography and mass spectrometry – for some samples, the replicates also includes repeated sample pre-processing, i.e. brucite coprecipitation. Each n corresponds to five bracketed measurements of the sample. We clarify this in the revised version (Section 2) and have added a footnote to the data table.

P6413, L23-26: *I don't understand the uncertainties provided for samples when $n = 1$. Did the authors ascribe a long-term external reproducibility of 0.12 pmil as I understood from the*

text? Then why are there some error values in table 1 varying from 0.12 to 0.21 pmil when n = 1?

We ascribed 2SD external reproducibility to samples analysed once, except in the rare cases where internal 2SD was larger than this, in which case we reported the larger internal 2SD value. This is the reason for the varying 2SD values in Table 1. We now adopt this same procedure for all samples (since we report 2SD uncertainty in the revised manuscript), and clarify this in a footnote to the table.

Discussion

P6419, L1-5: *At 58°S, there is little agreement between the mixing line drawn from end-members (15m and 428) and the intermediate values (215 and 107m). Although the authors point this out in the legend, it would need further discussion.*

As the figure caption states, the lines are not intended to be mixing lines, but rather to draw the reader's eye to the sense of variation between depth and the surface at both stations. Note that the winter mixed layer is, indeed, well-described as a mixture between the subsurface and the base of the summer mixed layer at both stations. It appears that at 58S, there is additional complexity within the summer mixed layer, which results in the apparent discrepancy the reviewer mentions. Any discussion of this feature would be very unconstrained and would not add to the manuscript, so we have chosen not to discuss this further, but have edited these sentences to better reflect the associated complexity.

P6419, L5-7: *The 20-25% contribution of surface water to Si in WML is a value very similar to the one already estimated by Fripiat et al. for the Southern Ocean (2011 a,b). This should be underlined.*

Thank you for pointing this out. This change has been made in the process of incorporating the Supplementary Material B into this section (see response to comment on Suppl. Mat. below).

P6419, L12-15: *...The link between high d30Si value of silicic acid in WML and low d30Si of exported opal is not obvious. Please clarify.*

To clarify this, we have added an additional sentence at the beginning of this paragraph.

Section 5.2: *The authors could start to discuss here Beucher et al. (2008) results, which complement their data further north.*

We now refer to the similar observations by Beucher et al 2008 in the first sentence of Section 5.2.

Section 5.3: P6424, L23-26: *Provide the mixing parameters used by the authors to find an influence of NADW <0.05 pmil on CDW (volume mixing fractions, silicic acid contents and Si isotopic signatures).*

As we clarify in the new Supplementary Material C, this result is calculated using the distribution of the quasi-conservative tracer PO_4^* , following Broecker et al., (1991, GBC). This tracer can be used to determine the volume fraction of NADW, f_{NADW} . We then draw on Broecker et al. (1991) and de Souza et al. (2012, GBC) for [Si] and $\delta^{30}\text{Si}$ values of CDW and freshly-ventilated NADW to estimate the $\delta^{30}\text{Si}$ value expected from mixing. As the new supplementary figure S8 clearly shows, this variation is very small, generally below $\sim 0.05\text{‰}$, because even though values of f_{NADW} range up to 0.6, the low [Si] of NADW means that its contribution to the dissolved Si pool is an order of magnitude smaller, such that its effect on CDW $\delta^{30}\text{Si}$ values is insignificant.

Section 5.3: ...[the authors] should check with simple stats whether these new data cancel out the differences highlighted in Fripiat et al. while taking into consideration their own uncertainties. Merely looking at Fig. S7 is not convincing.

We agree with the reviewer. The statistical argument made by Fripiat et al. (2011b) using a t -test (which ignored analytical uncertainty) is confirmed by a Monte Carlo t -test and a Monte Carlo Mann-Whitney rank sum test (performed since dataset normality is marginal; $p_{\text{Lilliefors}} \sim 0.15$), implying a difference between the Australian and Atlantic datasets compared by Fripiat et al. (2011b). We remain unable to explain this difference, and our data do not confirm the mechanisms that Fripiat et al. (2011b) proposed for its creation. Firstly, our eastern Pacific sector data do not exhibit a $\delta^{30}\text{Si}$ offset from the Australian sector data, contrary to the offset predicted by Fripiat et al. (2011b) due to the accumulation of low- $\delta^{30}\text{Si}$ opal in the ACC. Secondly, our mixing calculations (see response to comment above) indicate that the influence of NADW cannot be invoked to explain a higher $\delta^{30}\text{Si}$ value in the Atlantic sector, in contradiction to the hypothesis of Fripiat et al. (2011b). This implication is upheld by our Indo-Atlantic sector data. Nonetheless, as the reviewer points out, our high-latitude dataset is limited. We have thus rewritten the first paragraph of Section 5.3, such that it now highlights the associated complexities and uncertainties.

Figures and Supplementary Material

Fig. 6: *Ideally use more contrasted symbols and/or colours to help better differentiate the two latitudes.*

Changed.

Fig. 7: *Plot the sampling locations on this figure.*

Good suggestion. This change has been made.

Supplementary Material A & B: *These sup. mat are only a few lines each. They describe standard practices and provide key and easily understandable information. I suggest putting them in the main text.*

We have moved Supplementary Material B to the main text of the revised manuscript (Section 5.1), but retain the details of the Monte Carlo t -test in the Supplementary Material (relabelled B), rather than unnecessarily cluttering the main text in the already rather busy Results section.

Fig. S3: *Could the authors indicate on the figure the dates corresponding to their sampling for each station in order to directly indicate the timing of the sampling in comparison with biomass?*

Good suggestion. We have altered the figure.

Table 1: *For future reference and in light of the data ancillary, it could be useful to also provide $d^{29}\text{Si}$.*

Our $\delta^{29}\text{Si}$ and $\delta^{30}\text{Si}$ data are always linearly correlated, since we completely resolve all isobaric interferences. Thus, the $\delta^{29}\text{Si}$ data do not contain any additional information and can be easily calculated from $\delta^{30}\text{Si}$ data (e.g. Reynolds et al., 2007, JAAS), so we see no need to include them here.

If ODV software has been used to produce some figures, appropriate credit should be given.

Thanks for pointing out this oversight. Schlitzer (2009) is now cited in the caption to Fig. 2, and the *Ocean Data View* imprint is retained in all other figures created with ODV.