

# ***Interactive comment on “Exploring interacting influences on the silicon isotopic composition of the surface ocean: a case study from the Kerguelen Plateau” by N. Coffineau et al.***

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Reply to the reviews:

After reading the two reviews we can clearly see the main weakness in the manuscript as presented- the model, by necessity, is driven by time-series data available for the KERFIX site at the edge of the Kerguelen Plateau but, as there are no isotope data available from this site, we had to use the isotope data from the Kerguelen Plateau itself to consider whether or not the model was behaving realistically. This confused both of the reviewers, who both seemed to want the model curves to go perfectly through the isotope data which also, as noted in the publications that presented them, were

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Printer-friendly Version

Interactive Discussion

Discussion Paper



clearly heavily influenced by the complexities of circulation and particle export (and possibly also particle resuspension) on the relatively shallow plateau. When we revise the manuscript, we will address this issues and make it more clear that the point of the model, rather than to reconstruct the silica cycle on the plateau exactly itself, is tied to the KERFIX site at the periphery of the plateau. The model is then used to look at (as we have done in the paper) RELATIVE changes in  $d_{30Si}$  throughout the year and the implications of these findings for how we interpret the  $d_{30Si}$  of the surface ocean and of BSi. Because the way we have been thinking about it, while not wrong per se, totally overlooks that for most of the year, the Rayleigh or continuous input models we apply DO NOT APPLY because during most of the year there is not net ongoing drawdown of silicic acid concentrations.

We will also add a few sensitivity tests (by varying the  $d_{30Si}$  of the WW, by somehow turning off BSi production "during the winter", and by changing the fractionation factor for BSi production), although we would like to point out that there were several sensitivity tests in fact presented in the discussion paper (ie runs with and without fractionation during dissolution, runs with and without input from basalt dissolution, runs with different values for the  $d_{30Si}$  of DSi input from basalt dissolution). We're not sure why the one reviewer did not recognize these as sensitivity tests. We anticipate that the addition of the sensitivity tests will add a couple of figures to the manuscript and a couple of paragraphs of text.

More specific replies to the reviewers: Referee #2

Referee #2 brings up a number of useful points that we will address when we revise the manuscript. It is difficult to parse out the reviewer's points from the stream of thoughts, but here are our responses to the points we were able to identify:

- 1- We will add a data table containing the data from the CTD profiles.
- 2- Why present the new data when the study is largely a modeling study? We have presented the new data because they (and CTD profiles 1, 4, and 6 in particular)

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expand the geographic range of the data available for Si isotopes in the Southern Ocean. In addition, they serve to illustrate the general snapshot of Si isotopes with depth in the Southern Ocean, something that is worth illustrating before presentation of the model considering the behavior of Si isotopes dynamically over the course of an entire year.

3- The pooling of the CTD samples into, as the reviewer says, "layers" was in no way meant to imply an equivalence between CTD sites. The reviewer has not understood that in fact, this identification of which water masses the data belong to at each site allows us to better see what the differences might be in the processes that are going on at each site. Thus we identified samples of surface water, Winter Water (the water between the seasonal thermocline and the deepest depth of winter mixing), and Circumpolar Deep Water. These water masses are subjected to similar processes at the different locations. For surface water, this would be things like advective and diffusive mixing with winter water, loss of DSi (and fractionation of Si isotopes) to removal by diatoms, and recycling of DSi from dissolution of biogenic silica. For the non-surface water masses, these processes would be mixing with bordering water masses, mixing within the water mass, and the input of DSi from dissolution of sinking biogenic silica. Thus it is useful to group the samples by water mass in order to see the extent to which the  $d_{30}\text{Si}$  values are changing (or not) from site to site as the water masses move through the Southern Ocean.

4- The data used for input to the model are from the Kerguelen Plateau and environs as explained on p. 11412. For Si isotopes, as stated, the WW value used as the source for the DSi input to the mixed layer, the 1.6 ‰ value represents an average between values from the KEOPS dataset and our CTD 8. Because of the large range in  $d_{30}\text{Si}$  of WW both with depth and, most likely, seasonally as well (both things because at the top it is mixing with surface water and at the bottom it is not), it is likely that the exact value varies seasonally and geographically. Without a lot more seasonally resolved data than has been collected so far, however, we cannot pin that precisely down and

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hence used this constant value of 1.6 ‰.

5- If we, the authors, were looking for a single explanation (rather than the process responsible or set of processes cumulatively responsible) for the low d30Si values at DSi concentrations  $<20 \mu\text{M}$  (Fig. 4), we would not have built the model to track the effects of all the different processes affecting surface water d30Si throughout the year. The low values are odd and it would be nice to have some ideas why we're seeing them. And, in fact, the model has revealed an unexpected but significant answer. In fact, they are not odd at all, but the result of a switch from bloom growth (net drawdown of nutrients) which pushes up d30Si while lowering DSi, to net growth which is not fast enough, relative to diffusive inputs of DSi from the WW, to result in continuing net decrease in DSi concentrations. In this case, even at low DSi concentrations, the surface values can have the lower d30Si values more closely resembling WW than highly DSi-depleted surface waters during the bloom season. This is the key finding of this paper! It isn't necessarily due to fractionation during dissolution or because of input from basalt dissolution as hypothesized in previous publications.

6- There is no reason why areas away from the LIP that is the Kerguelen Plateau would be heavily influenced by basalt dissolution... although there is this general idea emerging (currently without Si data to assess it properly in terms of the silica cycle, for it is hard to collect such data) that weathering of lithogenic material on ocean margins could be providing considerable DSi to seawater. When we did this work, we were also highly skeptical of published claims that basalt dissolution was heavily influencing the Si isotopic composition of waters on the Kerguelen Plateau. We would like to be clear: we are not proposing nor advancing this hypothesis, merely critically examining it, something which needs to be done. Unfortunately, our results are largely inconclusive given the lack of data on the d30Si of DSi released during submarine basalt weathering. But that is a key point that also needs to be published, as it has been overlooked in previous estimates of the contribution of basalt dissolution to DSi on the Kerguelen Plateau. And fractionation of Si isotopes during all low-temperature submarine weathering is a

Full Screen / Esc

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Interactive Discussion

Discussion Paper

big problem that needs addressing if we are to truly close the Si isotope budget of the ocean.

7- When we revise the paper, we will add more  $d_{30}\text{Si}$  data from surface waters from the Kerguelen region versus day of the year, as suggested, although there are not many more data to add. However, such a plot will be of limited use (see the data of Fripiat et al plotted on Fig 7, for example) because there are so few data available and because these small number of data cover sites all over and along the edge of the Kerguelen Plateau there is a lot of local variability locked up in them that will serve to mask the temporal variability. Likewise the mid-late summer data were taken during a different year than the late summer/early autumn data. And, in terms of their place on the yearly calendar, they are spaced over no more than about 8 weeks of calendar year. Until there are true and proper seasonally resolved data from a specific location (such as a time-series site), a plot like this will probably confuse rather than clarify the patterns that occur.

8- Because Sutton et al's paper on variability in the fractionation factor came out after we did the model simulations, the effect of shifts in the fractionation factor with diatom assemblages was not considered in our work. As the reviewer states, as there is no information available on seasonal shifts in diatom assemblage, and because the Sutton et al work was limited to a small number of species, we really can't yet constrain how the average fractionation factor associated with diatom utilization of  $\text{DSi}$  will vary throughout the year. It might have a large effect. It might have little effect at all. However, in terms of Fig 4, if the diatom assemblage dominating at low concentrations of  $\text{DSi}$  (ie  $<20 \mu\text{M}$ ) had a significantly different (ie significantly less) fractionation, we would still expect the  $d_{30}\text{Si}$  of  $\text{DSi}$  increase with decreasing  $\text{DSi}$ . A shift in the fractionation factor (or variability in the fractionation factor) cannot explain the results in Fig 4 that we seek to explain. However, we will add a sensitivity test with different fractionation factors and perhaps a paragraph of discussion of this point about species specific fractionation to the discussion in the revised manuscript.

Full Screen / Esc

Printer-friendly Version

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Discussion Paper

9- Indeed, we have no idea if or to what extent submarine weathering of basalt will be seasonally variable. That is why we tried two different things, one of which was more seasonally important than the other. Let us be again clear, we are skeptical of claims that basalt weathering provides a significant amount of DSi to this region and don't really believe that it should show up in the Si isotopic signal. That we tried different ways of controlling the basalt input was us trying to give the basalt inputs as fair a shake as possible in our assessment of them.

10- The model and KERFIX average DSi agree within a couple of  $\mu\text{M}$  of each other and the BSi by a couple of  $\mu\text{mol L}^{-1}$ . By our reckoning, our variable mixed layer depth 1-box model is doing a smashing job of simulating the silica cycling in the surface water here. One could always play around and "tune" the DSi uptake and growth rate parameters and the sinking and dissolution of BSi (optimizing them so that they give the "correct" concentrations of DSi and BSi throughout the year), but while any particular combination of daily variable values for these parameters might yield the "correct" concentrations, it does not mean that the sets of values chosen for the variable parameters are realistic. We stand by our use of the constant values that anyway yield remarkably good cohesion with measured results. The early autumn peak of 2  $\mu\text{mol L}^{-1}$  in BSi that the reviewer mentions is related to the increased growth of diatoms as the ML begins to deepen after summer stratification and nutrient depletion. It may not show up strongly in the 5-year averaged KERFIX dataset, but it is a frequently observed (and classically recognized) feature of strongly seasonal systems in the ocean.

11- Fig 7- We disagree with the reviewer. Fripiat et al's data for DSi are within about 0.2 or 0.3 ‰ of our prediction based on the day of the year. There is more variability in the BSi, although as the reviewer notes, Stn 5 is bang on the curve. Given the local variability in  $\delta^{30}\text{Si}$  shown by Fripiat et al's data (which reflects in part the complex circulation and the differential retention of material at different locations on the plateau), how exactly does the reviewer envision the model output matching the data better? It is worth noting that the use of this model, as with a great number of models, is not

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with their reproduction of absolutely exact results from an extremely limited dataset, but with their illustration of the overall effects of processes (like mixing and biological uptake of DSi). We are only saying that this model does a good job of simulating the Si cycle in the Kerguelen region and that this Si cycling is similar in general principle to what happens in other strongly seasonal locations. The biggest value of the model output is what it tells us about the relative changes in  $d_{30}\text{Si}$  of DSi and BSi throughout the year in response to changes in the balance between mixing and productivity.

12- As explained on p 11416, the dissolution rate of dead diatoms was linked to the specific dissolution rate of 0.035  $\text{d}^{-1}$  and took into account the sinking velocity of the biogenic silica, something which was itself linked to the concentration of biogenic silica, and the depth of the mixed layer. Thus there was not a set fraction of BSi that dissolved per time step, but rather the fraction of BSi that was dissolving was related to how long dead diatoms were hanging around the mixed layer before being exported. This is a strategy deployed by other models (see Nugraha et al 2012) on top of being more sophisticated than just allowing a constant fraction to dissolve.

13- To take 0.2 ‰ into account or not. Every little bit counts. We'll soften the statement about what the paleoceanographers should do, but we won't go so far as to say they should ignore the idea that fractionation during dissolution, if it is real (and I think the jury is still slightly out on that) could lower the  $d_{30}\text{Si}$  of surface waters by 0.2 permil. Some cores only vary by about 0.6 ‰ between the LGM and the present day!

14- We don't understand why the phrase "an assumption that is unlikely to be true" is confusing. We will swap in the word "correct" for "true" if that helps. We were just pointing out that the assumption of the perfectly proportional release of Si and Nd from basalt during basalt weathering (and the secondary mineral formation that likely goes along with it) is probably a bad one. Perhaps the trouble is that the reviewer is unfamiliar with the concept of congruent dissolution.

15- Yes, it should be Fig 8b.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

16- Fig 1- We will refer the readers to Fripiat et al 2011 for that diagram.

17- DSibst We will add the definition of this abbreviation to Table 3.

18- 30Si instead of d30Si on the figs- Not sure what happened here. The delta fell off somewhere between our files and the proofs and we didn't catch it. Thanks for pointing it out.

The other reviewer General comments

The reviewer, stating that the model must be trusted on the basis of the "presented run" (in the singular) appears to have missed the very obvious fact that quite a number of runs are presented, with and without several key features of the model. This would hardly qualify as us requiring the readers to take a single model run for granted. However, we accept that we could have presented a few other sensitivity tests, and we will present them, briefly, in the revised version of the manuscript.

(i) See responses numbered 10 and 11 to Referee #2. One huge part of the problem with using the Kerguelen Plateau DSi and BSi isotope data to assess the performance of the model is that the model is tuned to the behavior of the mixed layer at the KERFIX site, just offshore of the plateau, and the plateau itself is a relatively shallow environment of fairly complex circulation, leading to considerable variability in the standing stocks of BSi, concentrations of DSi, and isotopic composition of both at any given point in time. The comparison was never meant to show a perfect correspondence, only that the model is yielding reasonable values for that general (and highly variable) part of the world. The match would be better if there were isotope data for the KERFIX site itself, but there are not. The KEOPS isotope data set and a couple of data points from our own lab are really all that there are to work with as a point of comparison. In a sense, this is the point of the paper the two reviewers struggle with the most, and obviously something we did not adequately clarify in the text. The mixed layer depth and temperature data used to drive the model are available from the KERFIX site at the edge of the plateau, but not from a site on the plateau itself. Thus the model itself

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Interactive  
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Interactive Discussion

Discussion Paper





should be tested with data from the KERFIX site, but such data do not exist. The best we can do is offer the Kerguelen Plateau isotope data as a point of nearby comparison and in that respect the model and the data agree remarkably well. In this vein, the reason we constructed this model less to explain the Kerguelen Plateau specifically and more to understand how the early autumn values of  $d_{30}\text{Si}$  of DSi could be low at low concentrations of DSi, such as seen in the Kerguelen Plateau datasets, but not seen uniquely in these data sets. And, in general, we have tried to discuss the model results in terms of the relative behavior of the isotopes in the BSi and DSi pools throughout the year (when do they go up? when do they go down? are they in lockstep or can they be decoupled?) and what processes have an influence over them. In that sense, the model more than fulfilled its mission, opening our eyes to the fact that the currently used models (Rayleigh distillation and the so called continuous input model) only apply to times of net nutrient removal (which is to say, only during a small part of the year).

(ii) The data on Fig 7 are plotted by day of the year, which means the B5 data can't be moved "to the left" on the plot. It is also likely that due to high rates of vertical mixing on the plateau (Park et al., 2011), the "effective" time of year for these samples is further to the right on the plot, which would bring them more in line with our curve. It should be further noted that Fripiat et al (2011) observed that the  $d_{30}\text{Si}$  of BSi on the plateau was higher than that of the DSi, which is to say, entirely contrary to expectation given the discrimination against the heavier isotopes of Si during silica biomineralization. They concluded that, in essence, due to processes like dissolution and export of the BSi and refreshment of the DSi in the mixed layer by mixing, the isotopic signal of the BSi was not a perfect recorder of the silica cycling in the mixed layer. This is a major problem with samples of BSi from the water column- because of partial dissolution, episodic sinking events, and advection of the particles as well as changing rates of input of DSi to the mixed layer, these samples don't clearly reflect what has been going on in the local water column. The sediments, by integrating over longer time periods and larger areas, do better in this regard by smearing out a lot of this noise. We will add a brief discussion of these points to the paper.

(iii) Adding De La Rocha et al data to Fig 7- Their omission was an honest oversight, nothing diabolical. Agreed, they range from 1.7 to 2.3 ‰ which puts them slightly lower than the simulations presented. However, they also plot slightly lower than the Fripiat et al data which supports the general point that input from the WW through diffusive input of DSi to the mixed layer is lowering the d30Si of the mixed layer, even if winter growth of diatoms is occurring. But again, both reviewers appear to have missed the point that the model is illustrating general principles of the behavior of isotopes in this region and that, given the constraints of the data available, we are comparing apples and oranges somewhat and still coming up with similar answers.

(iv) The advice to use the plateau Winter Water value of 1.9 ‰ for the value of DSi input to the mixed layer is incorrect. It was previously noted by Fripiat et al (2011) on p 19 of their manuscript that it is more likely that the source of DSi to the plateau mixed layer is the 1.5 ‰ value of the WW from the high nutrient, low chlorophyll area just offshore of the plateau rather than the WW on the plateau itself due to the relatively short residence time of waters on the plateau (4 – 9 months). Our selected value of 1.6 ‰ is thus in fact more appropriate to use than the suggestion of 1.9 ‰.

(next point) We would be happy to expand the discussion of the general implications of the model and thank the reviewer for reminding us that the sedimentary assemblages are in fact generally not skewed towards the bloom species. We can also think about how to turn off the winter growth in the model to do that test. It will be hard to run the model for five years (without seriously changing its architecture at which point is it still a sensitivity test of the model?), though, if all the diatoms are allowed to die (ie not grow) during non-bloom times of the year.

Specific comments The specific comments are mainly fairly minor or repeat points addressed above. We will take them into account (and respond to them in the final response to reviewers) when we revise the manuscript.