

# **Interactive comment on “Processes controlling the Si-isotopic composition in the Southern Ocean and application for paleoceanography” by F. Fripiat et al.**

In the following referee comments are shown in italics and the response in bold.

## **Referee 1.**

*Overview. This manuscript presents silicon isotope results made on suspended biogenic matter across a range of depths for 7 stations located in the south Atlantic sector of the Southern Ocean. Fripiat et al. observe that changes in the silicon isotope composition of water and biogenic material samples are associated with strong south-north silicic acid gradient. They then model their results using a box approach, incorporating seasonal changes in productivity, to explain the results they obtained for end of the growth season.*

*Comment. 1) The silicon isotope data presented is of a high-quality and warrants publication. However, the model developed by Fripiat et al. has a number of issues that left me wondering if their model adequately represents the silicon isotopes results that they obtained. For instance, they say that their model "... seems to adequately reproduce the seasonal evolution of silicic acid and biogenic silica concentrations in the PFZ mixed layer (Fig. 5b; Moore and Abbot, 2000; Quéguiner and Brzezinski, 2002)". How about showing the reader the model does indeed replicate seasonal changes in silicic acid concentration by comparing model results to field results?*

First of all as the utility of the submitted model has been often questioned by the referees (poor comparison with the data, processes not well parameterized, ...), we would like to express why we believe that such exercise is useful. Over the last decade (Varela et al., 2004; Cardinal et al., 2005, 2007; Cavagna et al., 2011; Fripiat et al., 2011a, 2011b, this study), a large number of observations in the mixed layer has been collected (Figure 3 in the submitted version). The two available models, Rayleigh and Steady state, are not able to explain such isotopic distribution. Such disagreement has been already pointed out in Varela et al. (2004) and Cardinal et al. (2007) and would already be sufficient to justify such model development. We believe that the failures of the previous models result either of (1) a variation in the fractionation factor across the productive season and/or (2) a seasonal variation in the expression of the different isotopic effects (dissolution, mixing, ...). We acknowledge that the submitted manuscript was dealing much more with (2). In agreement with the referee 1 (next comment) option (1) will be more discussed in the revised version. For (2) our rationale was "is it possible with the available

knowledge of the Southern Ocean Si-biogeochemical dynamic to reproduce the observations, in keeping a parameterization as simple as possible?". The current knowledge of the Si-biogeochemical dynamic can actually be described quite simply: one productive/export peak (Pondaven et al., 1998; 2000; Honjo et al., 2000; Brzezinski et al., 2001; Quéguiner and Brzezinski, 2002) and an increasing dissolution : production ratio from 0 at the beginning of the growing period up to 1 at the end (Brzezinski et al., 2001, 2003; Beucher et al., 2004; Fripiat et al., 2011c). Our model is able to reproduce such dynamic and such simple parameterization seems to be able/enough to explain the observations (both high and low  $\Delta^{30}\text{Si}$ , Figure 7 in the submitted manuscript). The main objective was to investigate the link between the isotopic composition and the relative silicic acid utilization, for an application in paleoceanography. This is clearly not an attempt to better constrain the complexity of the seasonal silicon cycle or to do some quantitative estimates.

To answers to the comment (1), with this sentence, the idea was to simulate adequately the timing of the different isotopic effects, to see their seasonal expression in the isotopic balance (previous paragraph). With this perspective and the current knowledge of the Southern Ocean system, our model clearly achieves this aim (Pondaven et al., 1998; Brzezinski et al., 2001).

The only time series showing the silicon biogeochemical dynamics in the Polar Front Zone is the study of Brzezinski et al. (2001) in the Pacific sector (Figure 1; PFZ between 61°S and 52°S). Both the timing and the magnitude of the variations are indeed respected in our model. Silicic acid concentrations in Brzezinski et al. (2001) start at 15-20 $\mu\text{M}$  to finish at <1 $\mu\text{M}$  (we start at 15 to finish close of 1 $\mu\text{M}$ , Figure 5b in the submitted manuscript). Biogenic silica peaks at  $\pm 5\mu\text{M}$  as in our model (Figure 5c in the submitted manuscript). Our gross biogenic silica production is a little bit higher than in Brzezinski et al. (2001; respectively up to 1 and 0.5 $\mu\text{M}$ ). Taking into account the snapshot nature of their gross Si-uptake measurements (24h incubation experiments), it's very likely to miss the Si-uptake maximum. Instead to directly compare such observations with the model (variability in the time axis for the different studied areas), we prefer to insert in the revised Figures 5 and 6 the range of the published observations (e.g. Brzezinski et al., 2001; Quéguiner and Brzezinski, 2002; Fripiat et al., 2011c).

*After reading the manuscript, Fripiat et al. imply that they have seasonal silicon isotope data for the region. If they do have silicon isotope measurements for water biogenic samples then it would be good to present these numbers as it would help validate the box model.*

We will provide in the revised article a new version of Figure 3 which is actually showing seasonal silicon isotope data for the Southern Ocean area, covering a significant part of the growing period (See Figure 1 enclosed in this reply which is the new Figure3; October to March; Varela et al., 2004; Cardinal et al., 2005, 2007; Fripiat et al., 2011a, b; Cavagna et al, 2011). These data compiled from the literature are not originating from the region. In addition, such a large area implies an inherent significant variability in (1) the initial conditions, (2) the timing

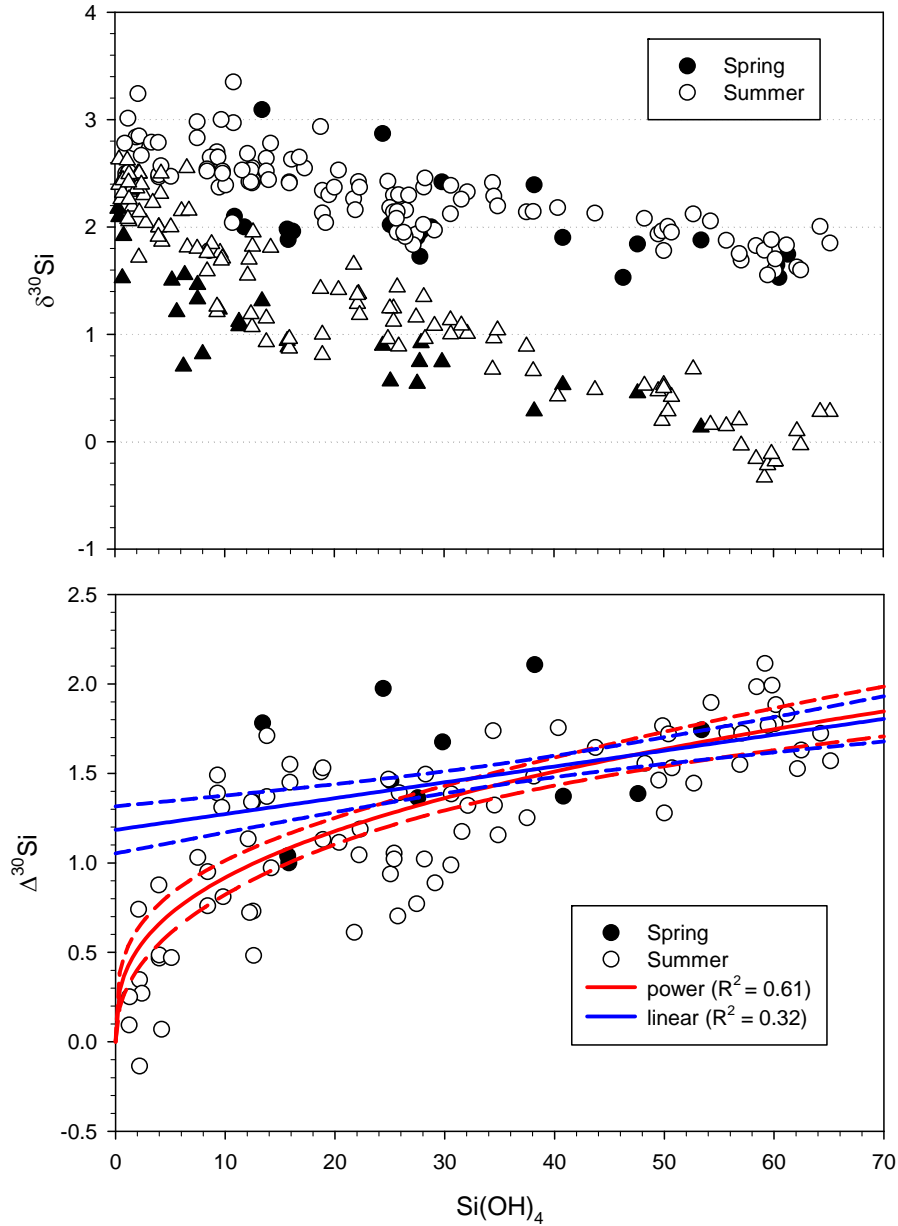


Figure 1: Panel (a) Mixed layer  $\delta^{30}\text{Si}$  (both for  $\text{Si}(\text{OH})_4$ , circles, and  $b\text{SiO}_2$ , triangles) vs.  $[\text{Si}(\text{OH})_4]$  for the SIZ-WG, AZ, and PFZ. Panel (b) Mixed layer  $\Delta^{30}\text{Si}$  vs.  $[\text{Si}(\text{OH})_4]$  for the SIZ-WG, AZ, and PFZ (data from BGH: this study; AESOPS and SOFEX: Varela et al., 2004; CLIVAR-SR3: Cardinal et al., 2005, 2007; KEOPS: Fripiat et al., 2011a; EIFEX: Cavagna et al., 2011). The linear regression line in panel (b) is for the  $\Delta^{30}\text{Si}$  larger than 1‰ (blue line with 95% confidence intervals). The power regression line in panel (b) is for all  $\Delta^{30}\text{Si}$  data (red line with 95% confidence intervals).

and (3) the magnitude of the productive peak. For such reasons it is difficult to directly compare the model, describing one case study (here the polar front zone across BONUS-Goodhope transect), with the overall compilation. Since it appears this was unclear, we'll clarify this in the revised version to avoid a reader believing that we have seasonal isotope data for the region.

*I suppose my main concern with the box model is that there are only a couple of silicon isotope tie points to constrain the model - day 0 and day 90 - it would be helpful to present data across the growth season so that one can get a better comprehension of the process(s) that are important in the development of silicon isotope composition of the dissolved and solid phases.*

We agree with the reviewer however such data are not available so far to the best of our knowledge. A simple parameterization of the seasonal silicon cycle is already able to explain the disagreements between the previous models (Rayleigh and Steady State) and the observations. See also our previous answers regarding the objectives of our model.

*2) The trend of increasing isotope fractionation between the water and solid phase Fig. 3b. is similar to the trend observed by Wille et al. (2010) for sponge spicules (note that they expressed their values as the solid minus water). They explored silicon isotope fractionation model that included silicon isotope fractionation during silicic acid uptake, silicon polymerization and silicon efflux from the cell. This model is based on the one presented by Milligan et al. 2004 for diatoms. I would encourage Fripiat et al. to explore this model to explain their data. It could turn out to be the first conclusive explanation for variable silicon isotope fractionation between the solid and aqueous phases in diatoms. Not that this model has also been used by Hendry and Robinson 2012 to describe silicon isotope fractionation in diatoms and sponges. Fripiat et al. also might want to comment on the recent paper presented by Sutton et al. at the AGU fall meeting where they observed varying silicon isotope fractionation factors for Southern Ocean diatoms.*

In the sake of clarity for following discussion, here are the two discussed equations:

$${}^{30}\epsilon_{net} = {}^{30}\epsilon_{inf} + \frac{\rho_{eff}}{\rho_{inf}} \cdot ({}^{30}\epsilon_{poly} - {}^{30}\epsilon_{eff}) \quad (\text{Milligan et al., 2004})$$

$${}^{30}\epsilon_{net} = {}^{30}\epsilon_{inf} + \left( 1 - \frac{(V_{max,P} \cdot [Si(OH)_4] / K_{Si,P} + [Si(OH)_4])}{(V_{max,I} \cdot [Si(OH)_4] / K_{Si,I} + [Si(OH)_4])} \right) \cdot ({}^{30}\epsilon_{poly} - {}^{30}\epsilon_{eff}) \quad (\text{Wille et al., 2010})$$

where  ${}^{30}\epsilon_{net}$ ,  ${}^{30}\epsilon_{inf}$ ,  ${}^{30}\epsilon_{eff}$ , and  ${}^{30}\epsilon_{poly}$  are respectively the isotopic fractionation of the whole cellular metabolic balance (net fractionation factor), the influx of silicic acid into the diatom cell, the efflux of silicic acid out of the cell, and the polymerization of silicic acid into biogenic silica. The  $\rho_{eff}$ ,  $\rho_{inf}$ ,  $V_{max,P}$ ,  $V_{max,I}$ ,  $K_{Si,P}$ , and  $K_{Si,I}$  are respectively the efflux flux, the influx flux, the maximum specific rates of polymerization, the maximum specific rates of influx, the half-saturation constant for polymerization, and half-saturation constant for influx. The equation of Milligan et al. (2004) implies a linear relationship between the efflux:influx ratio and the net fractionation factor. The equation of Wille et al. (2010), depending of the chosen values for the

kinetic constants – highly variable, implies a relationship or not between the silicic acid concentration and the net fractionation factor.

We decided first to not include such discussion in the submitted manuscript owing to the still large uncertainties on the cited processes and used models:

- The Efflux has never been measured in the Ocean, so it is impossible to compare with *in situ* data.

- The magnitude of the different isotopic effects has been never measured. For example, to observe an increase of the net fractionation factor with an increasing efflux:influx ratio, the fractionation associated with the polymerization ( $^{30}\epsilon_{\text{poly}}$ ) has to be larger than the one occurring during the efflux ( $^{30}\epsilon_{\text{eff}}$ ). Even if we can expect a larger isotopic fractionation associated with polymerization, owing to the larger associated phases changes ( $\text{Si}(\text{OH})_4$  to  $\text{bSiO}_2$ ), still large uncertainties remain: (1) the polymerization occurs inside a specific vesicle (the silicon vesicle deposit, SDV; Martin-Jézéquel et al., 2004) implying that to be expressed the isotopic fractionation associated with polymerization has to be associated with an additional efflux of silicon out of the SDV to the plasmalemma; (2) the phase changes associated with Si-transport and polymerization are still largely unknown (Martin-Jézéquel et al., 2004).

- Si-uptake seems to be, in most of the cases, relatively well described with a Michaelis-Menten saturable uptake kinetic (Nelson et al., 2001; Mosseri et al., 2008; Thamatrakoln and Hildebrand, 2008). Anyway, large seasonal and zonal changes have been observed in the kinetic constants, especially in the Southern Ocean (Nelson et al., 2001), giving difficult to impose only one pair of kinetic constants ( $V_{\text{max,P}}$ , and  $K_{\text{Si,P}}$ ) for the whole dataset in Figure 1b (as for sponges; Wille et al., 2010; Hendry and Robinson, 2012). No information exists for the kinetic constants associated with efflux (if efflux can be described with a saturation function). The figure 2b we provide here shows that the relative values between kinetics constants have significant implications for the outfit of the relationship between silicic acid concentration and net fractionation factor. To observe a decrease in the net fractionation factor with decreasing concentration (as in Wille et al., 2010; Hendry and Robinson, 2012; and this study), the kinetic constants have to be larger for the influx. Again such rationale could appear to be logic but there are no way to check such statement.

- The only way to fit the model of Wille et al. (2010; e.g. Figure 2b in Hendry and Robinson, 2012) with the figure 1b is to assume no isotopic fractionation with influx and a large fractionation associated with polymerization (Figure 2a). We believe that this goes against the observations since: (1) in the Figure 2b of the submitted manuscript,  $\Delta^{30}\text{Si}$  in the SubAntarctic and SubTropical zones is larger by 1‰ despite low silicic acid concentration; and (2) a significant isotopic fractionation imprint on  $\delta^{30}\text{Si}_{\text{Si}(\text{OH})_4}$  is observed in areas where low silicic acid concentration prevails all year (Reynolds et al., 2006; Beucher et al., 2008; GEOTRACES intercalibration exercise in the Sargasso Sea). Since at low silicic acid concentration, the Si-efflux has to be minimal (Thamatrakoln and Hildebrand, 2008), the observed starting isotopic fractionation has to be set by the Si-influx, the transport of silicic acid inside the cell (Milligan et

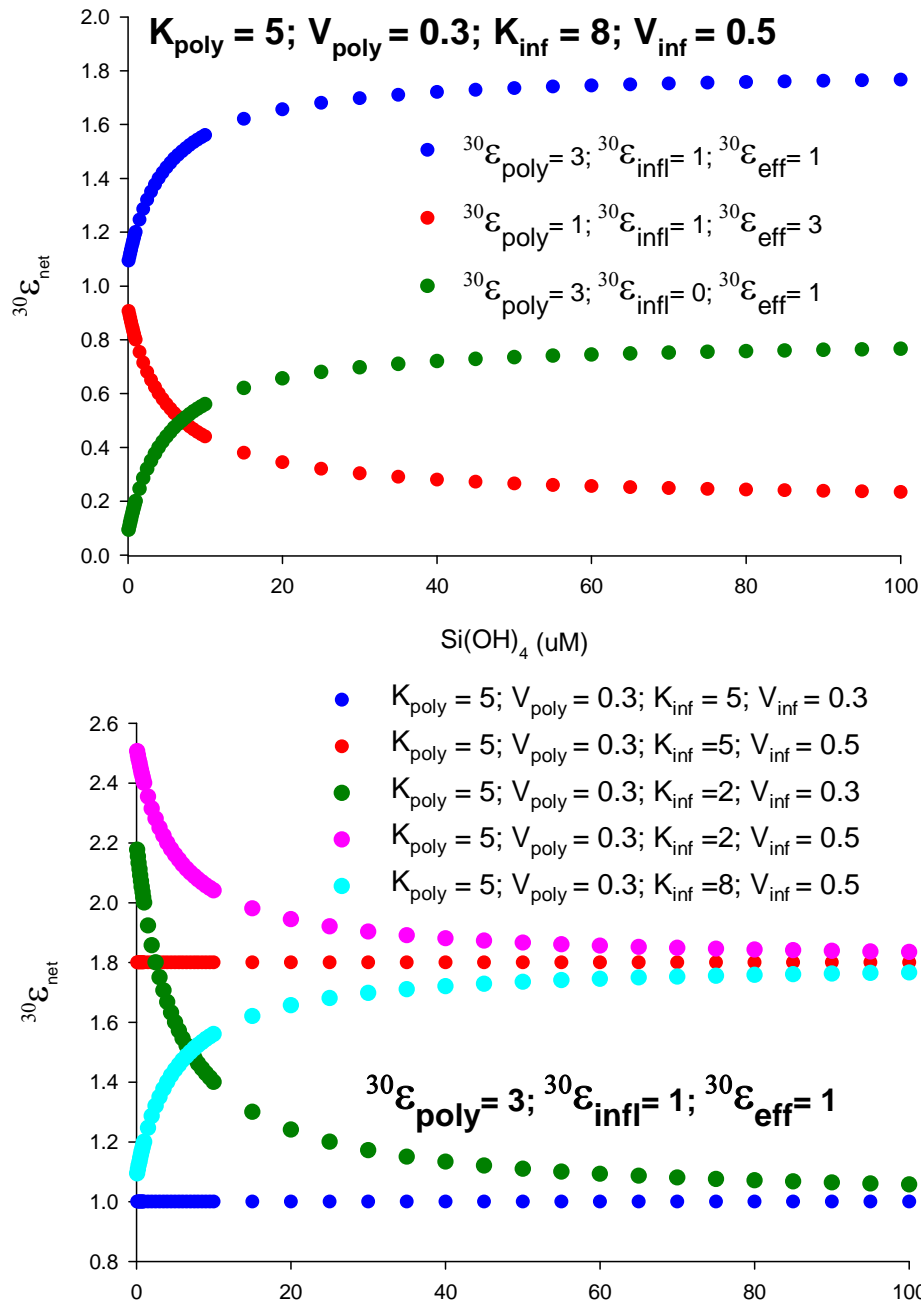


Figure 2. Relationship between the net fractionation factor and silicic acid concentration, following the model of Wille et al. (2010) for the sponges. Panel (a): model outputs by varying the magnitude of the different isotopic fractionations. Panel (b) model outputs by varying the kinetic parameters.

al., 2004). If no fractionation is associated with influx, the net fractionation factor should be close to 0 at low silicic acid concentrations. For such reasons, we believe that additional processes can be at stake to explain such observations. The more pronounced trend at low silicic acid concentration can simply also indicate that the resulting small silicic acid pool is more

easily affected by additional process, such as mixing and dissolution (in order to fit the power regression line in the Figure 1b).

Following the reviewer comment, we propose in the revised version to take into account and discuss more these potential variations in the fractionation factor. Our rationale would be:

- To discuss the resemblance between the curves ( $\Delta^{30}\text{Si}$  vs.  $[\text{Si}(\text{OH})_4]$ ) in this study with the ones for the sponge studies (Wille et al., 2010; Hendry and Robinson, 2012, e.g. Figure 2b in Hendry and Robinson, 2012), but shifted  $\Delta^{30}\text{Si}$  at low silicic concentrations toward  $\pm 0\text{‰}$  instead of  $\pm 1\text{‰}$ . Such observation is in disagreement with the  $\Delta^{30}\text{Si}$  distribution and isotopic imprint in the dissolved phase at low latitudes where low silicic acid concentration prevails all year (this study, Reynolds et al., 2006; Beucher et al., 2008; GEOTRACES intercalibration exercise in the Sargasso Sea).

- We would point out the linear correlation between  $\Delta^{30}\text{Si}$  and silicic concentrations for the  $\Delta^{30}\text{Si}$  larger than  $1\text{‰}$  (expected values for minimal isotopic fractionation associated with influx; Figure 1b). Such correlation could be explained by an increasing effl:inf ratio at high silicic acid concentration (Milligan et al., 2004; Thamtrakoln and Hildebrand, 2008).

- The  $\Delta^{30}\text{Si}$  lower than 1, observed only at the end of summer, can be partly due to a fractionation during  $\text{SiO}_2$  dissolution. Following the equation given by Demarest et al. (2009), such process can explain only half of the variability in the  $\Delta^{30}\text{Si}$  lower than 1 (see also Figure 7a in the submitted manuscript). The particularly low values at low silicic acid concentration imply another process. We suggest that the low silicon uptake:supply ratio at the end of productive period together with (a) depleted mixed layer and (b) large vertical silicic acid gradient could be responsible for the other half.

- We agree that a source of variability could be an inter-specific variation in the fractionation factor. This would be also discussed in the revised version.

*3) Is silicic acid in the STF region sourced from waters moving northward out the subAntarctic zone (SAZ) across the subAntarctic Front (SAF)? Beucher et al. (2007) found that the silicon isotope composition of sedimentary opal north of SAF in the southern Indian Ocean did not originate in SAZ "The sub-Antarctic does not appear to be the major source of  $\text{Si}(\text{OH})_4$  to the subtropics". Could this be the same in figure 2b? If so then the decreasing trend  $\delta^{30}\text{Si}$  versus latitude is only valid for sample south 45 degrees.*

Sarmiento et al. (2004) did suggest an indirect source from the SAZ to the STZ, via the SubAntarctic Mode Water and subsequent vertical mixing with SubTropical thermocline but such transport takes several years. Indeed water particles in the different cited areas spent several years before to exit each zone (Sokolov and Rintoul, 2007; 2009). Consequently they are taking

part to several winter mixings, the process setting the initial conditions for the mixed layer. The dynamic described in Beucher et al. (2007) implied a simple advection by Ekman transport from the SubAntarctic to the SubTropical Zone with no re-setting of the initial conditions in winter. It seems for us in disagreement with the actual knowledge of the Southern Ocean dynamic.

The fact that there is a decreasing trend versus latitude implies a relationship between the latitude and the isotopic composition only, not the source. Subsequently the statement that there is a decreasing trend of  $\delta^{30}\text{Si}$  vs. latitude is still valid (Figure 2 in the submitted manuscript).

*Minor comments.*

We agree with most of the minor comments so we will integrate them in the revised version. The disagreements are mainly with the minor comments associated with the previous general comments.

### **Referee 2.**

*I would suggest to clarify these points: 1. what is mixed in line 24 page 10158?*

We believe that it is on page 10157. It is silicic acid via vertical mixing. We will clarify this in the revised version.

*2. please define the depth of the mixed layer*

This would be added on Table 1 (determined using a combination of threshold density/temperature criterions; Table 1 in de Boyer Montégut et al., 2004).

*3. what is the degree of overlap with the Fripiat 2011a paper? I think that some information is missing in the current paper based on the assumption that the 2011a contains all important info.*

Fripiat et al. 2011a describe the  $\delta^{30}\text{Si}$  distribution of silicic acid across the complete water column profiles. No isotopic data on biogenic silica are provided. Water masses dynamics in the Southern Ocean is suggested as the main driving processes for this distribution. So the first paper is focused on the “global” Southern Ocean circulation affecting the whole water column and relationship with the main water masses. The present submitted paper present an additional set of unpublished data on  $\text{bSiO}_2$ , including the very first oceanic deep profiles of  $\delta^{30}\text{Si}$  in suspended particles. It is focused on biological and physical processes affecting the biogenic silica isotopic distribution, with a strong emphasis on surface processes. Nevertheless, we understand the rationale behind the referee’s comment. In the sake of clarity, more details would be given in the revised version when a connection is done between these two papers.



4. section 4.1.1 - looks to me that 100 m is too shallow according to your Si data. please explain.

Following the combination of threshold density/temperature gradient to estimate the mixed layer depth, the latter has been estimated to lie between 80 and 95m. Subsequently, only the data above 95m would be taken to estimate final summer mixed layer composition.

However for the depth of the mixed layer in the model, we need to be representative of the whole growing period. Faure et al. (2011; Figure 7b) estimated for this area a mean mixed layer depth of 100m for both the Polar Front Zone and the Antarctic Zone. The estimation seems to be more difficult for the SubAntarctic Zone, owing to the large scatter of the data (from 0 to 200m). However, 100m seems to be not a reasonable estimate for the mean SAZ summer mixed layer (Figure 7b in Faure et al., 2011). This would be more discussed in the revised manuscript.

5. where are the data to determine  $15 \pm 11 \mu\text{M}$ ?

We agree with the referee that, as it was presented, there was no way to check the statement (see the answer to the comment 3). We suggest to insert a Table with the initial and final conditions. Consequently we would also give more details about the choice of such values.

We suggest a slight variation in the way to represent the initial conditions. In the submitted version, the initial conditions for the Polar Front Zone was the Antarctic Intermediate Water ( $14 \pm 11 \mu\text{M}$ ) which includes some waters north of the SubAntarctic Front. We would limit the initial estimation to each specific zones. Subsequently, the halocline in the Polar Front Zone would be taken as to be representative of the initial condition.

6. how do you model a season when the data is only relevant to 1 month (at the end of the bloom).

See the answer to the comment 1 of the referee 1.

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