Topical Editor Decision: Publish subject to minor revisions (review by editor) (03 Aug 2021) by <u>Andrew Yool</u> Comments to the Author: Dear Authors,

Thank you once again for your manuscript revisions and responses to referees.

Given the significant criticism levelled by one referee, and the specific and detailed points raised in their review, I returned the manuscript to them for an evaluation of your revisions.

In reply, the referee is broadly pleased with your revised manuscript, and finds that it addresses much of their criticism. Nonetheless, they still identify a significant lack of clarity in the description, and rationale, of the dissolution parameterisation used. As this aspect of your model is a key determinant of its operation and skill, having clarity in details of its formulation is highly important.

To this end, I am returning the manuscript to you to address these remaining points from your referee. As ever, should you have any questions about the referee's remarks, please feel free to get in contact with me and I will endeavour to have them clarified.

Finally, please accept my apologies for this extended review process of your manuscript.

With best regards,

Andrew Yool.

Dear Dr. Yool,

Thank you for coordinating this review of, and for the preliminary decision on, our manuscript. Please see Reviewer comments given in blue font, and our responses provided in black font, with changes to the manuscript reproduced in red font.

One of the new points arises from confusion, where it seems the reviewer did not see in the last rebuttal where I explained some of the flux numbers were outdated and replaced- over the past year I have continued to tune the parameters of the model and there was a stage where new plots were added but the table was not updated, which was the source of the original confusion and for which I would like to apologise. Since the last revision the table is consistent with the plots, but the reviewer apparently did not notice this statement in the rebuttal.

But I would like to thank the Reviewer for pressing the point about inconsistent opal fluxes. Upon examination I found that the model diagnostics output was not correctly reporting opal export, dissolution and sediment losses applied at model runtime. This has been fixed and the simulations have been re-run, with new data files and model code uploaded to the GEOMAR data repository. New figures have also been created for the manuscript and the text adjusted accordingly (in red font).

And we have tried again to represent the opal dissolution coded into the model in a form that is understandable to readers. I am sorry this equation (32) has produced such confusion!

You might be interested to know that a first paper has been published using this model: Saini et al. (2021) Southern Ocean Ecosystem Response to Last Glacial Maximum Boundary Conditions, Paleoceanography and Paleoclimatology https://doi.org/10.1029/2020PA004075

Best wishes, Karin Review of the revised version of "Explicit silicate cycling in the Kiel Marine Biogeochemistry Model, version 3 (KMBM3) embedded in the UVic ESCM version 2.9" by Kvale et al., submitted to Geoscientific Model Development in 2021

Main comments and recommendation

This is the second version of this manuscript that I review, and the authors have taken many of my comments to the previous version into account. My two main points of concern about the last version were unclear or wrong explanations in the model description and inconsistencies in the described global Si fluxes and the comparison with observation based estimates. I still think these two points need a bit of work, and so I would recommend that the manuscript should be further revised before it can be published.

We apologise for both the wrong presentation of model equations and for the confusion arising over inconsistent fluxes. As explained in the last rebuttal, the fluxes had not been updated after a switch to a better parameter set. Also an error was found in the model diagnostics. These problems are corrected here.

While most of the remaining unclear points in the model description are rather minor, one concerns a central part of the manuscript, the implicitly treated dissolution of the sinking opal. As it is one of the main points of the manuscript that this formulation of opal dissolution improves the modeled global silicic acid distribution, this is an important point.

Several biogeochemical ocean models use model-specific temperature-based formulations of opal dissolution. We tried 2 of them (Gnandesikan 1999, Enright et al. 2014) and neither produced acceptable silicate distributions, probably because the parameters applied were adjusted to their different model physics. Which is to say, we are not the first to use an approximation that works for our model (reducing the importance of our particular parameterisation, which might or might not be portable to other models). Explicit dissolution will be implemented over the next months, so this first approximation is meant as a 'placeholder' and also to provide a benchmark on performance as the code is improved in the coming years.

The dissolution of opal is described in equation 32. The equation has changed with respect to the last version by the multiplication with depth (z) within the flux divergence term on the right hand side, so that now the production Pr(Opal) and dissolution Di(Opal) have the same unit, which makes sense. In the manuscript is is stated that the unit of Di(Opal) is mol Si m^{-3}, but I think, as it is a rate, it should be mol Si m^{-3} yr^{-1}.

Yes, that is correct. It should be per day and this is now corrected in the text (Line 232).

But more importantly I still do not understand the rationale behind equation 32, for two reasons:

- Is the chosen form of the flux compatible with a reasonable assumption on the implicit vertical distribution of sinking opal, or of the sinking flux? I do not think so. As a simple example, assume an ocean with uniform temperature (which is a good approximation to the ocean below 2 km depth). Then the immediate consequence of eq. 32 is that opal dissolution Di(Opal) is constant throughout the water column. If the concentration of opal decreases with depth (as it must, because of dissolution), then that would imply that the dissolution rate needs to increase with depth. Or, if the dissolution rate is constant, then opal concentration must also be constant vertically. Of course, the chosen temperature dependence will lead to a decrease of the scaled flux (the quantity within the d/dz) with depth, and thus to a more realistic vertical behaviour of the flux. But it still remains unclear to

me how the proportionality of the flux to depth z can follow from an assumption on the steady-state vertical distribution of opal biomass and dissolution rate.

We can not plot the vertical distribution of sinking opal because we do not model this quantity explicitly. However we find that our parameterization produces an average export rate of opal that decreases with depth. In so doing, observed dissolved silica distributions are reasonably reproduced.

We had some internal discussion about how the equation is represented and apologise for how confusing this equation has been. We have tried again, and hope that it now makes sense to readers. Its actually very similar to Gnandesikan (1999) Eqn 2. I think my earlier attempts to represent it were overly complicated.

- Also, if the parameterization in eq. 32 would be compatible with a vertical distribution of sinking opal, then it would automatically follow that the integral over the total water column dissolution would be smaller or equal to the integrated production, independent of the chosen dissolution rate and its temperature dependence. In the current formulation, however, this is not the case: Here it has to be ensured (probably by making lambda small enough) that the flux (scaled by the vertically integrated total production) at the bottom of the ocean lambda*depth/w * exp(T/Td) is not larger than one.

We apologize if the Reviewer thought we needed to artificially constrain the dissolution to be less than production. This line of code is in place just to be sure in the case of numerical instabilities, but it is not required. But, we have removed the sentence from the manuscript which we had added as a response to this point in the last rebuttal in order to avoid confusing readers. (As a note to the Editor: it seems this point is referring to a point made in the previous review, to which we responded by adding a sentence that seems to have only confused our answer. This new sentence is now removed.)

I think the authors should discuss the relationship of their chosen flux parameterization to assumptions on sinking speed and the vertical distribution of opal. Probably this cannot be done in a strict analytical way (with a temperature-dependent dissolution rate, an analytical solution for a steady state flux profile is hard to derive). But a qualitative idea why this flux profile was chosen should be possible.

We have added some text to the manuscript addressing opal flux (Line 235): Opal dissolution in the water column is primarily controlled by temperature and silicate saturation, with higher temperatures and lower silicate saturations leading to faster dissolution (Sarmiento and Gruber, 2006; Ridgwell et al., 2002). Secondary drivers include the aluminium content and surface area of diatom shells (Van Cappellen et al., 2002), and the presence or absence of organic coatings, where the loss of the coating increases opal dissolution rates (Bidle and Azam, 1999, Van Cappellen et al., 2002). We do not consider silicate or aluminum concentration dependencies explicitly in this model because we do not explicitly calculate thermodynamic dissolution of opal (nor do we simulate aluminium), but the temperature dependency exerts an influence on dissolution of the same sign (faster dissolution in warmer, i.e. shallower and undersaturated, water).

My other main criticicm of the last manuscript version were inconsistencies or confusing statements on the global Si fluxes. The authors have changed their notation now to Tmol Si/yr, which makes the comparison with the numbers in Treguer et al, 2021 easier. But in doing so, also some of the stements on numbers have also changed, and to me it was really unclear now how the different terms are defined:

The statements had to change because the values had to change because the dataset underlying the statements changed- we updated the model with a new parameter set 2-3

revisions ago, which somewhat improved model performance compared to the originally submitted dataset. Unfortunately the figures had been updated but the table had not. We apologise for the inconsistency, which has caused confusion. Now the table values are consistent with the figures.

- In the new manuscript (line 338-340 and table 6) it is said that the total opal production is 127.9 Tmol Si/yr, which would be low against the estimate of 255+-52 Tmol/yr in Treguer et al., 2021. But in the previous manuscript version the total production was stated as 7.68 Pg Si/yr, which approximately translates to 270 Tmol Si/yr, close to the Treguer et al. estimate. So, was the old number simply a miscalculation? There are more differences in numbers between the old and the new manuscript version, e.g. in the stated total dissolution. Is this due to a different way that the term has been defined?

No, it is an updated model output which was converted to Tmol Si/y. Table 6 numbers are now consistent and replaced with a new set of values from the latest simulation.

- I also do not understand the relation between production, water column dissolution and sediment export of opal. If we take the statement from the new table 6 of total opal production of 127.9 Tmol Si/yr, and substract the total opal water column dissolution of 64.4 Tmol Si/yr, the difference (63.6 Tmol/yr) does not dissolve in the water column and hence must be deposited on the sediment. How is that compatible with the statement at the vertical flux of opal at 2000 m depth is only 19.46 Tmol Si/yr? Does that mean that more than two thirds of the opal deposition into the sediment happen above 2000 m depth, i.e. on the shelves?

Note Table 6 values have changed from previous drafts of the manuscript following a rerunning of the model after finding a problem with opal flux diagnostics. We thank the reviewer for pointing out some inconsistencies in the opal budget, which are now corrected. According to the estimated global silica budget by Tréguer et al. (2021) about 40% of opal burial occurs in the continental margin. Our model currently produces about 69% removal at the seafloor above 2000 m depth, which might be too high (though there is a lot of uncertainty about processes like downslope transport and how much opal is actually transported into the deep ocean along the bottom, and we do not model sedimentary exchange, burial, preservation, distinguish between coastal and open ocean, etc). This is a useful benchmark as we improve our model.

I think the authors should try to make it possible for the reader to close the opal budget by stating a) how the total production of Si is distributed between the upper 130m and deeper, b) how much of that production dissolves with the layers 0m-130m, 130m-2000m, and below 2000m, c) how much opal is deposited into the sediment within these three layers, and d) how much of the deposited opal is permanently buried within these layers.

We have now included the requested information in Table 6. Comparison with previously published budgets is more straightforward on a global basis, because, e.g., neither of the Tréguer et al. 2013 and 2021 reviews distinguish depth levels in this manner and our model is missing relevant processes (i.e. coastal processes, reverse weathering, sponges, does not distinguish between coastal zone/open water, etc., and has a low spatial resolution).

Minor comments

- line 82-83, "any opal that reaches the seafloor is replaced by external sources": This contradicts the formulation of the simple sediment scheme (lines 266 ff.), where it is explained that only a fraction of what arrives at the seafloor is permanently buried and needs to be replaced by external sources to keep the inventory stable. Please clarify.

The sentence is modified to read (Line 82): "any opal that is lost to the seafloor is replaced by external sources"

- in my last review I suggested to replace the word 'bioavailability' for the Michaelis-Mentenkinetics-like term in nutrient uptake. This has been done. The replacement 'uptake' (lines 107, 115, 117, ..) is, however, equally misleading: the quantity that is described is a dimensionless limitation term, uptake would imply some material change, probaby in mol/volume/time.

These instances have been changed to 'limitation', or reverted to 'availability' as per the instructions of an earlier Reviewer (Lines 106,115,117,126).

- On line 117, it is said that the nutrient limitation terms for nitrate, phosphate and silicic acid are multiplied with the maximum potential growth rate. This is a bit misleading because it suggests a multiplicative limitation by the different nutrients; later on (eq. 13) it is clarified, that only the minimum of the limitation terms, not their product, is used.

The nutrient limitation terms are in fact multiplied with the maximum potential growth rate. Those resulting products are then compared, with the minimum selected. The language is changed to "the minimum nutrient limitation term" (L118)

- in equation 8, the two numbers given are not pure numbers, but should have a unit, namely that of a silicic acid concentration. I would suggest these numbers are replaced by a symbol, and that these numbers with their proper units are then added to the parameter table. Besides, I had already mentioned in my last review, that writing a decimal number as 8E-4, when you mean 8 times 10 to the power of minus 4 is something that fortran understands, but that is violating typographical conventions.

The units are provided for all numbers in Eqn 8, see L126, "with constants given in the same units". We prefer to leave the values in the equation, as this is not our equation (it is from Aumont et al., 2003) and it is easily recognizable in its present form. We have now changed to exponential notation.

- the description of the dependency of the initial slope of the PI curve and on the ChI-a:C ratio on the degree of iron limitation is correct, but could use a bit more justification. The neglection of the dependency of the ChI:C ratio on the light level is justified here, I believe, because in the model, ChI is really only needed in the surface layer (to calculate photosynthesis rates and to compare with satellite estimates), and not at depth, where the dependency on light becomes crucial.

This equation is not new to this model. We prefer to focus discussion on the parts which are new and unique, and offer a reference to Nickelsen et al. (2015) which describes the equation in greater detail.

- In line 159, the temperature-dependent fast remineralization is called 'respiration', in contrast to the linear mortality. It is maybe a bit picky, but while from an ecostem perspective bacterial consumption is a respiration, from the phytoplankton perspective I would rather describe it as excretion (because it is originally dissolved organic carbon that is excreted and then respired by the bacteria).

The parameterisation is identical across phytoplankton types and has been described as "respiration" in previous UVic model publications, but we have removed "respiration" and shortened the sentence (L 161)

- in line 162-163, the quadratic mortality is called 'non-grazing mortality' and contrasted with a self-grazing term GZ. Again it is maybe a bit picky, but to my knowledge the quadratic zooplankton mortality (the so-called closure term, Steele and Henderson, 1992) is exactly meant to represent grazing by higher trophic levels. See Edwards and Yool (2000) for a discussion of the different forms of closure.

We have not modified our zooplankton equation, other than to add diatoms as a new food source. This equation has been published with other versions of UVic (e.g., Nickelsen et al., 2015). But it does appear to be inconsistent with the quadratic mortality function found in Edwards and Yool (2000), and we thank the Reviewer for pointing this out. The language used in the manuscript text was also incorrect, and has now been changed to (Line 162): In addition to mortality from higher trophic level predation calculated with a quadratic mortality function ($m_z Z^2$), intra-guild predation is represented with a separate term (G_z). This parameterization of zooplankton mortality will need to be investigated in the future, as there are plans in the UVic user community to modify the grazing formulation as well.

- equation 21 contains several numbers, but some of the numbers are meant to have units (the 8 should be 8 mmol m⁴-3), while others are pure numbers.

Units have been added to the 8.

- line 198: 'organic carbon' should probably be 'organic nitrogen'

This has been corrected.

- in equations 27 and 27, should the iron scavenging rate not also depend on the concentration of (organic and CaCO3) particulates? Also, the term [Fe]prime is not defined. It probably means the concentration of 'free' inorganic Fe (often denoted [Fe']), probably calculated from total dissolved iron and ligand concentration, but this is not stated. I also do not understand why the prime is shown here with letters, instead of Fe', as is the conventional usage.

We used the same notation as Nickelsen et al. (2015) so that readers would know it is the same model. But we have now changed to Fe' and have also defined the term. Also we apologize the detritus and carbonate terms had been left out of the equations, which is now corrected.

- in equation 30, the production of opal is made proportional to the mortality of diatoms, which makes sense, but one term is missing, namely the 'bacterial loop' mortality term (mu* x DT). What happens with the opal produced by diatoms that die by that pathway?

As with CaCO3, opal produced by diatom losses to the bacterial loop are not considered. This is because, the bacterial loop recycles only in the upper ocean and very rapidly, so a fast exchange of dissolved-to-particle forms should not significantly influence the distribution of opal down the water column. It might be worth looking into this assumption once explicit dissolution is implemented.

- line 223-224: it is unclear whether in 'average surface opal:free detritus export value of 1' the detritus is meant in units of N or C. My guess is that the 'value' (rather a 'ratio', I would say) is meant to be in Si:C units, which implies a Si:N of larger than 6, in the range of observations.

The units are now specified.

- But that made me wonder: what is the non-limiting Si:N ratio implied by equation 31? If Si>kSi and Fe>kFeDT, the Si:POC ratio is 0.5 and hence a Si:PON ratio is around 3. This seems high to me, as Si:N in most diatoms under non-limiting conditions is about one.

We adopted this parameterization from Aumont et al. (2003) and cite their paper as the original reference. Note that the kSi value is also dependent on the ambient Si concentration. A PhD student is currently testing this aspect of the model (the Si:N ratio) and will prepare a manuscript on it in the coming months.

- the authors have chosen to keep their habit to put some terms in square brackes, which have a meaning of a rate of change of a concentration (e.g. on the right-hand side of equation 39). Of course the authors are free to use any notation that they want, but I reiterate that this notation is a) inconsistent with the conventional usage of square brackets in chemical texts, where the square brackets mean 'concentration of', i.e. [Fe] = concentration of Fe, and b) that it is used inconsistently: In equation 31, for example, [Fe] means concentration of Fe in micromol/m^3, while in eq. 35 [Fe]_sed means a flux in micromol/m^2/yr, and in eq. 39 [Fe]_col means a rate of change of concentration in micromol Fe/m^3/yr.

We appreciate the concerns of the reviewer on this, but these changes were explicitly requested by an earlier reviewer, who has approved the manuscript.

- in eq. 38, again, the two numbers are not pure numbers, but have a unit.

Units are now provided in the equation, rather than only in the text

- in eq. 42, the alkalinity change is assumed to be proportional to the phosphate change with a proportionality factor of -R_C:P. I do not understand the rationale for that factor. Yes, biogenic phosphate and nitrate uptake change alkalinity. In Wolf-Gladrow et al., 2007, it is stated that "assimilation of 1 mole of nitrogen (atoms) leads to (i) an increase of alkalinity by 1 mole when nitrate or nitrite is the N source, (ii) to a decrease of alkalinity by 1 mole when ammonia is used, and (iii) to no change of alkalinity when molecular nitrogen is the N source" and "Uptake of 1 mole of phosphate (H3PO4, H2PO4, HPO42–, or PO43–) by algae in accordance with the + nutrient-H -compensation principle increases alkalinity by 1 mole per mole P (...). Please note that the change of TA is independent of the phosphate species taken up by the cell". So I think the proportionality factor should be rather minus (Redfield ratio between N and P plus one).

We thank the Reviewer for finding this error in our equation. It should read R_N:P. The equation has been corrected.

References:

Edwards, A. M., & Yool, A. (2000). The role of higher predation in plankton population models. Journal of Plankton Research, 22(6),1085–1112. https://doi.org/10.1093/plankt/22.6.1085

Steele, J.H. and Henderson, E.W. (1992) The role of predation in plankton models. Journal of Plankton Research, 14, 157–172.

Wolf-Gladrow, D. A., Zeebe, R. E., Klaas, C., Körtzinger, A., & Dickson, A. G. (2007). Total alkalinity: The explicit conservative expression and its application to biogeochemical processes. Marine Chemistry, 106(1-2 SPEC. ISS.), 287–300. https://doi.org/10.1016/j.marchem.2007.01.006

We thank the Reviewer for providing these references.