

Interactive comment on “Ocean carbon and nitrogen isotopes in CSIRO Mk3L-COAL version 1.0: A tool for palaeoceanographic research” by Pearse J. Buchanan et al.

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Response to Reviewer 2 (Christopher Somes)

Christopher Somes had some specific questions and comments before publication of the manuscript could be recommended. These relate to our treatment of biological fractionation in the carbon isotope routine and some issues with our interpretation/discussion of results of both $d^{13}C$ and $d^{15}N$.

— Page 7, lines 9-13: Biological carbon fractionation. There should be more discussion justifying why you only account for a species effect and not aqueous CO_2 concentration

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(Popp et al., 1989; Rau et al., 1989) and/or phytoplankton growth rate (Laws et al., 1995). There are of course large uncertainties, but there seems to be some general relationship with aqueous CO₂ so I am surprised that this is not included in a model designed for palaeoceanography.

We have implemented this functionality and we are currently running experiments to quantify the effect of a “variable” fractionation factor (Laws 1995 relationship) versus fixed at 21 per mille. We expect these experiments to come to equilibrium state within a month.

— Page 8: N₂ fixation fractionation. Since N₂ fixers have a lower $\delta^{15}\text{N}$ value than the atmospheric N₂, this implies some fractionation right? Does the $\delta^{15}\text{N}$ value go into diazotrophs biomass and then remineralize or go directly into NO₃?

Yes N₂ fixers do actually fractionate when fixing N₂ to NH₄ that is then incorporated into biomass and I suppose our wording here is misleading. We have corrected the sentence to illustrate that while N₂ fixers do fractionate during their conversion of N₂ gas (with a $\delta^{15}\text{N}$ of +0.7 per mil (Klotts & Benson, 1963)) to NH₄ that is incorporated into biomass (typically with a value of -1 per mille), we implicitly account for these transformations by specifying the end product.

"Because we simulate NO₃ and ¹⁵NO₃ as tracers, our calculations require solving for an implicit pool of ¹⁴NO₃ during each reaction involving ¹⁵NO₃. The introduction of NO₃ at a fixed $\delta^{15}\text{NNO}_3$ of -1 ‰ due to remineralisation of N₂ fixer biomass provides a simple example with which we can begin to describe our equations. Setting the isotopic value of newly fixed NO₃ to -1 ‰ is simple because it removes any complications associated with fractionation. We note, however, that in reality the nitrogenase enzyme does fractionate during its conversion of aqueous N₂ (+0.7 ‰ to ammonium, and that the biomass that is subsequently produced can vary substantially depending of the type of nitrogenase enzyme used (vanadium versus molybdenum based) (McRose et al., 2019). However, we choose to implicitly account for these transformations and con-

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siderably simplify them by setting the $\delta^{15}\text{N}$ of N_2 fixer biomass equal to -1‰ which reflects the more common Mo-nitrogenase during N_2 fixation (Sigman and Casciotti, 2001). A $\delta^{15}\text{NNO}_3$ of -1‰ is equivalent to a $15\text{N}:14\text{N}$ ratio of 0.999 in our approach where 0‰ equals a 1:1 ratio of $15\text{N}:14\text{N}$. If the amount of NO_3 being added is known alongside its $15\text{N}:14\text{N}$ ratio, in this case 0.999 for N_2 fixation, we are able to calculate how much 15NO_3 is added. The derivation is as follows. We begin with two equations that describe the system."

— Page 9, lines 5-20: NO_3 utilisation. Please show the model equation used for the calculation of utilisation in the model (i.e. "u" in equation 15) since it is not straightforward exactly how this is calculated.

We have added an additional equation and information in the paragraph to describe what this utilisation factor is and how we calculate it.

— Page 10, Table 1: UVic model. Although the model is based on UVic, the University of Victoria group has not been involved in the C13 and N15 development. Please replace "UVic" with "UVic-MOBI" (Model of Ocean Biogeochemistry and Isotopes) and "University of Victoria" with "Oregon State University/ GEOMAR Kiel".

Corrected.

— Page 10, line 22: "Weak undercurrents that are important for reducing nutrient trapping at the Equator". Strong undercurrents and so-called nutrient trapping occur in the upper kilometre (mostly upper 400 meters), whereas your largest bias is between 1500-3000 meters, so something is missing here. I guess the main problem is that you switch off organic matter remineralisation when oxygen runs out which allows the organic matter to sink and remineralise much too deep? If so, this should be pointed out here.

We have added a sentence that makes the reader aware of our treatment of organic matter remineralisation.

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"Alternatively, the expansion oxygen minimum zones could be due to our conservative treatment of organic matter remineralisation (appendix A), where remineralisation will not occur when O₂ and NO₃ are limiting. Excess, unremineralised organic matter therefore falls deeper in the model in the oxygen-deficient zones."

Also, we are currently running a new experiment where this conservative remineralisation scheme is turned off to assess the effect.

— Page 11, lines 3-7: "... far exceed reconstructions of Eide et al., (2017) .. it is possible that the upper ocean values of Eide et al., (2017) underestimate the preindustrial $\delta^{13}\text{C}$ -DIC field". I think the robustness of the reconstruction deserves a discussion paragraph if you are going to raise this point. Perhaps there is reason to be somewhat sceptical of this reconstruction in the upper ocean. One important aspect I think they have not accounted for is the anthropogenic effect on biological uptake and remineralisation. My C13 model simulations predict this anthropogenic effect lowers $\delta^{13}\text{C}$ by 0.5 per mil in the Pacific at 700 meters (compare "Modern" versus "Preind" differences at 15 μM NO₃ in Figure 3 of Glock et al., (2018)), which is due to phytoplankton incorporating the lighter anthropogenic CO₂ and remineralising at depth, whereas their reconstruction suggests basically negligible anthropogenic effect at these depths. Note this effect is required for my model's ability to reproduce the range of modern observations there (see Figure S5 in Glock et al., 2018) and becomes even more important as approach the surface. Do all of the models significantly overestimate these upper ocean values? It would be really interesting if you could also run a hindcast simulation forced by observed decreasing atmospheric $\delta^{13}\text{C}$ CO₂ and reproduce the modern observations. If so, I think you would have a legitimate argument that errors/uncertainties in the reconstruction may be significantly contributing to the large model-data misfit. I leave this up to you if it is feasible to accomplish, but I believe it is an important issue to discuss if this dataset is going to be the standard for model comparison. That said, I still believe your decision not to include an aqueous CO₂ dependency in your phytoplankton carbon fractionation is also likely contributing to your overestimated $\delta^{13}\text{C}$ DIC,

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since that reduces phytoplankton fractionation in the warm open ocean gyres.

First, we agree that the underestimation of $\delta^{13}\text{C}$ in the upper ocean in the Eide 2017 dataset is likely due to a neglect of biology introducing low $\delta^{13}\text{C}$ DIC via remineralisation.

Second, thank you for the reference to the Glock et al., 2018 paper. It certainly does seem that the 0.5 per mille offset near the surface (15 μM NO_3) between your PI and Modern simulations fits with the offset between the models in this study and Eide reconstruction.

Third, while it is not feasible to run hindcast/historical simulations for this study, we think that the bulk of evidence from the four models shows that the upper ocean Eide reconstruction is likely biased low, owing to the neglect of the biological introduction of low $\delta^{13}\text{C}$. Replicate figures of Figure 3 (previously figure 2) for each model are now included in a supplement.

The following alterations to this paragraph have been made: "All models performed most poorly in the Atlantic Ocean, with poor correlations, high variability and greater biases, and all models predicted upper ocean $\delta^{13}\text{C}_{\text{DIC}} \geq 2.0$ ‰ (Supplementary Figures S1, S2 and S3) which further suggests that the upper ocean values between 200 and 500 metres of (Eide et al., 2017) may be too low. The underestimation of $\delta^{13}\text{C}_{\text{DIC}}$ may be due to a neglect of biology introducing anthropogenic, isotopically depleted carbon to surface and subsurface layers in the Eide et al. (2017) reconstruction."

— Page 12: Figure 2 Something seems to be wrong with your color bar scale as it does not match the contours, which I assume are correct.

True! We have corrected the figure. We have also added the same figures but for the different models to the supp material.

— Pages 13-15: Denitrification parameterisations. It is important to be more transpar-

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ent about the artificial parameterisations to account for known model biases on both water column (i.e. NO₃ reduction value) and sedimentary denitrification (i.e. amplification) in the main text. I have no problem including them, but I think it is fair to at least briefly note the effect they have on your simulations (e.g. how much the global rates changes because of them). It is not really a fair comparison to include models that include these artificial parameterisations (COAL) to models that don't (your chosen version of UVic-MOBI, PISCES). For example, our following paper with UVic-MOBI (Somes et al., 2017) with improved nitrogen cycle dynamics including sedimentary amplification better reproduces global mean del15NO₃ similarly to COAL. It is not important which version of UVic-MOBI you decide to include, but these key denitrification parameterisations in COAL should be stated in the main text given its importance for del15N. I would argue that if water column denitrification cannot react naturally to climate-induced changes to oxygen and remineralisation, it significantly limits the model's ability as a tool for palaeoceanographic research from a nitrogen isotope perspective. This has led our group to implement physical parameterisations to better mimic equatorial undercurrent (Large et al., 2001; Getzlaff & Dietze, 2013), so we do not have to rely on this artificial water column denitrification reduction parameterisation anymore. This topic should be discussed.

The points raised are important and we have included a discussion of them in the text. We have aimed to be more up front about what the limitations of the model are.

We have added the following: "An important caveat to the del15NNO₃ routines of CSIRO Mk3L-COAL should be noted. CSIRO Mk3L-COAL underwent significant tuning of water column and sedimentary denitrification parameterisations in order to reproduce known values of del15NNO₃ during development. One important parameter is the lower threshold of NO₃ concentration at which point water column denitrification is shut off (section A2.3). In CSIRO Mk3L-COAL this is set at 30 mmol m³, which is an arbitrary limit that was implemented to prevent water column denitrification from reducing NO₃ to zero in the large suboxic zones. Hence, a caveat of the current model

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is an inability for water column and sedimentary denitrification to realistically adjust as suboxia changes. However, the parameterisation does allow for targeted experiments where the ratio of water column to sedimentary denitrification can be controlled if, for instance, it is unclear how water column and sedimentary denitrification respond to certain conditions. This is currently the case during the Last Glacial Maximum, where expansive suboxic zones in the Pacific (Hoogakker et al., 2018) were counterintuitively associated with lower water column denitrification (Ganeshram et al., 1995). We have, in this version, chosen to keep this parameterisation and note that future developments will involve an option to more realistically and dynamically simulate responses to variations in suboxia."

— Page 14, line 9: del15N in PISCES Please cite the paper that describes del15N in PISCES: I am unaware of any publication on del15N in PISCES.

There is currently no paper describing del15N in PISCES. The data was given to me by Laruent Bopp, who is currently working on a GMD paper for this purpose. I will include a citation of Bopp et al., (in prep) if this is agreeable to the editor/journal.

— Pages 17-24: Section 5. Ecosystem effects. I liked the sensitivity experiments focusing on a few key parameters/processes. However, I think they would benefit from an extra table (or two) that summarizes their key results. There are so many numbers mentioned directly in the text, I found it difficult to “digest” them all in a comparative context.

We have included a summary table of the major biogeochemical effects (table 5).

— Page 18: Variable stoichiometry. Please cite the key studies here and refer to the specific Appendix section that describes this so readers can quickly find it.

Completed. We have also added similar pointers in the other ecosystem experiment sections.

— Page 37: Acknowledgements. Will your published code and model output be acces-

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sible to the public.

Yes. The code is already accessible via the link in the Code Availability section. The data is being placed in an online repository for public access on the National Computational Infrastructure in Australia, which will be minted with its own doi.

Interactive comment on Geosci. Model Dev. Discuss., <https://doi.org/10.5194/gmd-2018-225>, 2018.

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