

Review of the first revised version of

“Southern Ocean controls of the vertical marine $\delta^{13}\text{C}$ gradient – a modelling study”

submitted for publication to *Biogeosciences*
by A. Morée and co-authors

1 General comments

1.1 Appreciation of the replies to reviewers

The authors have all in all well responded to the referees' comments, with two exceptions.

1. The questions raised by Anonymous Referee #2 about the weathering fluxes have only partly been addressed. Except for the average $\delta^{13}\text{C}$ signature of the DIC input from weathering, there is still no information regarding the *quantitative* constraints upon which the adopted weathering fluxes have been chosen (it would also be good to know their values).
2. In the response to Comment 2.2.3, I read that “In an open system, the sediment loss of nutrients and carbon over time will empty the whole ocean of nutrients, which would not give very meaningful results.” This cannot be correct. As explained earlier on, PO_4^{3-} is replenished by the (constant) weathering input. Upon perturbation, the model system adjusts its carbonate, organic matter and opal production and burial fluxes to evolve towards a new steady state where burial fluxes again match the input fluxes. The ocean will not run empty, as the production decreases with decreasing nutrient concentrations thus reducing the burial rates.

1.2 Appreciation of the revised manuscript

The authors have rewritten their manuscript to a large extent. The language has gained in precision and the presentation and discussion in depth. The literature review is adequate now and the study is much better brought into context with previous studies.

The model description has been improved. The separation between surface and deep ocean waters has been revised and is more consistent now. Extra details are now provided in the strongly extended Supplementary Information, which also includes extra graphs with relevant results.

The discussion has been revised and manuscript now also includes a figure with C-13 isotopic profiles for different ocean basins.

However, in some instances, the discussion of the results remains unnecessarily speculative: it should be possible to derive far more quantitative insight from

the model results. The analysis of the results ought to go further than currently done. It is, e. g., incomprehensible that the diagnosed decoupling of the deep-sea PO_4^{3-} concentration from $\delta^{13}\text{C}$ and $\Delta\delta^{13}\text{C}$ in the Southern Ocean nutrient depletion experiment is not analysed any further. I encourage the authors to better make out the reasons for this decoupling, because, as they – correctly – it offers an alternative to the usual proxy interpretation of deviations from the $\delta^{13}\text{C}:\text{PO}_4^{3-}$ relationship.

Finally, there are several troublesome errors in the paper. It is impossible that the weathering input of DIC has an average $\delta^{13}\text{C}$ signature of 14‰; it is also impossible for the ocean to degas CO_2 where the surface ocean $p\text{CO}_2$ is lower than $p\text{CO}_2^{\text{atm}}$; figures document CO_2 exchange fluxes in ice-covered regions, whereas the text states that ice cover blocks gas exchange. Please find details in the Specific Comments below.

Given these fundamental errors and inconsistencies in the paper — which unfortunately shed doubt on the validity of the rest of the paper as well — I cannot but ask for another major revision.

2 Specific comments

2.1 Model calibration/spinup and control state

2.1.1 $\delta^{13}\text{C}$ of weathering DIC input

In the manuscript (page 4, line 7 and also in the response to Comment 2.2.3), we read that “The $^{13}\text{C}/^{12}\text{C}$ ratio in the weathering flux would be equivalent to a $\delta^{13}\text{C}$ of DIC of 14‰.” There is something wrong with this 14‰ value. It is first of all completely unrealistic. The total sedimentary carbon subject to continental weathering has an average $\delta^{13}\text{C}$ of -5‰ ; the most abundant carbonate source has a $\delta^{13}\text{C}$ of $1.8 \pm 0.2\text{‰}$ (Derry and France-Lanord, 1996). Second, at steady state, this input requires a sink (or a combination of sinks) with globally equivalent characteristics. There is however no realistic combination of carbonate and organic carbon sinks that could lead to such a high average $\delta^{13}\text{C}$.

2.1.2 Control run: ocean-atmosphere $p\text{CO}_2$ gradient and air-sea CO_2 flux

There are contradictions in the reported results for air-sea exchange of CO_2 in the control run: in Fig. S4 (Supplementary Information p. 4), we see that there is a tongue-shaped area extending into the Atlantic Ocean in the Northern Hemisphere where the air-sea-flux of CO_2 is positive, while the $p_{\text{CO}_2}^{\text{oc}} - p_{\text{CO}_2}^{\text{atm}}$ difference is negative there, as can be seen in Fig. S3. This is a big flaw. Please check this!

2.1.3 Description and experimental design

Although the description of the model spin-up procedure has been improved it still lacks many important details. Except for the carbon isotopic signature of

the weathering flux, it is still not specified on what quantitative basis the weathering fluxes have been determined. We now read that there are weathering fluxes for DIC, alkalinity, phosphate and silica, and that these are fed in at a fixed stoichiometric ratio, but that is all that is provided as information (why not simply report the values of the fluxes?).

2.2 Results and discussion

2.2.1 Air-sea gas exchange rate experiments

This section remains one of the weakest of the study. Some parts are formulated in a vague qualitative style and provide little quantitative information (page 4, lines 5–20); others are long-winding, difficult to read and understand (page 4, lines 21–31). All in all the presentation and discussion of the results remain superficial and give an impression of a half-done job.

First of all, the $p\text{CO}_2^{\text{atm}}$ results presented in this section are to some extent counter-intuitive: increasing the gas exchange rate makes $p\text{CO}_2^{\text{atm}}$ increase; reducing the same rate makes $p\text{CO}_2^{\text{atm}}$ increase as well. In general, common sense would expect that opposite changes of the value of a model parameter lead to opposite effects, possibly except with strongly non-linear models; but even with non-linear models, this expectation should be met for sufficiently small perturbations of parameter values, except in very peculiar situations. A factor of four change can probably not be considered a small variation, so some non-linear behaviour has to be expected. In any case, I would consider deviations from this global scheme very suspect and would proceed to an in-depth analysis, starting with smaller perturbations (e.g., 50%, a factor of two) – finally there is no compelling reason for the particular choice of a factor of four. Here, these striking results are reported without any further ado. Strange enough, $\delta^{13}\text{C}^{\text{atm}}$ appears to behave as expected: increasing the gas exchange rate reduces $\delta^{13}\text{C}^{\text{atm}}$; decreasing gas exchange rates increases $\delta^{13}\text{C}^{\text{atm}}$.

Second, the discussion and analysis of the results consider only one half of the situation. The $p\text{CO}_2^{\text{atm}}$ increase at increased gas exchange rates is ascribed to a weaker Southern Ocean carbon sink. Unfortunately, not a single quantitative flux value is given to support this claim! Let us apply the reasoning to the rest of the world, following the same logic. At steady state (or, after 2000 years of simulation, at quasi steady-state), the global net exchange of CO_2 between the atmosphere and the ocean must be zero. If the perturbation experiment results present a weaker carbon sink Southern Ocean than the control run, it should also present a weaker carbon *source* elsewhere, most likely at low latitude. Following the same logic as before, a weaker carbon source to the atmosphere would be responsible for a *lower* $p\text{CO}_2^{\text{atm}}$. The conclusions that can be drawn from the kind of semi-qualitative argument that this discussion is based upon thus appear to be ambiguous, i. e., useless. Or there could be a stronger sink elsewhere (not mentioned though). Looking at sources and sinks is probably not the most reliable way to make out the mechanisms at work. What is sure, though, is that the global net exchange of CO_2 between the ocean and the atmosphere is zero at steady state. Assuming a globally uniform $p\text{CO}_2^{\text{atm}}$, we

then have

$$\sum_{i,j} A_{ij}(k_w)_{ij}(\text{pCO}_2^{\text{atm}} - (\text{pCO}_2^{\text{oc}})_{ij}) = 0 \quad (1)$$

where i and j denumber the grid elements, A_{ij} is the surface area and $(k_w)_{ij}$ the specific gas exchange coefficient at grid point (i, j) . Accordingly,

$$\text{pCO}_2^{\text{atm}} = \frac{\sum_{i,j} A_{ij}(k_w)_{ij}(\text{pCO}_2^{\text{oc}})_{ij}}{\sum_{i,j} A_{ij}(k_w)_{ij}}. \quad (2)$$

This holds as is for steady state under any of the air-sea exchange experiments with globally perturbed $(k_w)_{ij}$'s: if these are uniformly increased by a factor of 4 (or any other value), that value cancels out. The key to understanding the $\text{pCO}_2^{\text{atm}}$ changes lies thus in the distribution of pCO_2^{oc} , which in turn depends on the distribution of DIC and TA (assuming constant temperature and salinity). Gas exchange perturbations should have negligible impact on the TA distribution as long as the ocean-sediment exchange has not started to respond. So, it would be instructive to analyse how the surface ocean DIC distribution has changed.

Third, referring in this context to Fig. S4 to support the reduced Southern Ocean sink argument adds further confusion and is to some extent misleading. In Fig. S4 ice cover has not been taken into account! This is really a terrible shortcoming of that figure! As stated elsewhere in the text, the Southern Ocean south of 60 °S is permanently covered by ice, which completely blocks gas exchange. The green band in the Southern Ocean has actually no meaning (it should actually not be there). In the Southern Ocean north of 60 °S I am, unfortunately, not able to make out any significant differences between the exchange rates of CO_2 in the three panels. The total SO sink of atmospheric CO_2 appears to be quite stable to me—please feel free to prove me wrong, with adequate flux numbers, which could certainly be easily derived from the model results.

I do, however, see marked differences at low latitudes and they should be quantified in the discussion (e.g., integrated over a zonal band in the basin). And, by the way, it is not clear to me why Fig. S4 represents the situation after 100 instead of 2000 years.

To shed light on this confused situation, I have done some simulation experiments on my own with an ocean carbon cycle model, albeit of lower complexity than HAMOCC2s. First, I have performed a 120,000 yr control run, which was then continued by two 50,000 yr perturbation runs, mimicking fast gas and slow gas (using perturbations of the gas exchange constant by a factor of four). For what the results are worth and as food for thought, here is a summary of the results:

Experiment	after 2,000 yr			after 50,000 yr		
	$\text{pCO}_2^{\text{atm}}$	$\delta^{13}\text{C}^{\text{atm}}$	$\delta^{13}\text{C}^{\text{avg}}$	$\text{pCO}_2^{\text{atm}}$	$\delta^{13}\text{C}^{\text{atm}}$	$\delta^{13}\text{C}^{\text{avg}}$
Gas slow (/4)	289.4	-6.14	0.24	290.5	-6.29	0.15
Control	282.4	-6.53	0.25	282.4	-6.53	0.25
Gas fast ($\times 4$)	278.4	-6.77	0.26	277.7	-6.63	0.39

$\text{pCO}_2^{\text{atm}}$ is reported in ppm and $\delta^{13}\text{C}$ in ‰; $\delta^{13}\text{C}^{\text{avg}}$ is the ocean-atmosphere average $\delta^{13}\text{C}$; control run extended at steady-state.

As expected, opposite perturbations of the rate constant produce effects in opposite directions. After 2,000 years, about 80% of the $p\text{CO}_2^{\text{atm}}$ difference to 50,000 years is reached. There is some significant change in $\delta^{13}\text{C}^{\text{atm}}$ beyond 2000 years, related to global ocean $\delta^{13}\text{C}$ adjustments towards the new steady state: in the gas-fast experiment, low-latitude surface ocean $\delta^{13}\text{C}$ is reduced by 0.23–0.26‰ after 2,000 years, leading to the burial of carbon with lower $\delta^{13}\text{C}$ than at the end of the control run, and thus gradually increasing the system average $\delta^{13}\text{C}$. In the gas-slow experiment, the opposite happens (after 2,000 years, the low latitude surface ocean $\delta^{13}\text{C}$ is increased by 0.1–0.2‰, and as result of burial changes global ocean $\delta^{13}\text{C}$ decreases).

I would really recommend to run all of the experiments far beyond 2000 years. So many interesting things happen once the sediment feedback is allowed to come into play...

2.2.2 The biological pump: SO nutrient depletion

On page 10 (lines 14–17) we read that

This is interesting in light of glacial proxy interpretation, as deviations from the $\delta^{13}\text{C}:\text{PO}_4^{3-}$ relationship (Sect. 2) are usually interpreted as the influence of air-sea gas exchange on $\delta^{13}\text{C}$ (Eide et al., 2017b; Lear et al., 2016), but could thus also come from changes in nutrient uptake efficiency. As for a changed POC sinking rate, $\Delta\delta^{13}\text{C}$ is affected more in older waters (Fig. 4).

This is not only *interesting*. I would rate this as the *most important outcome* of this study. It is, unfortunately, not followed any further. No attempt is made to analyse this decoupling and to work out the contributing mechanisms.

2.3 Supplementary Information

As mentioned in section 2.1.2 above, there are problems with the model results reported in Figs. S3 and S4. Please check this.

3 Technical comments

Manuscript

Throughout the paper: please use the verb “to lower” (and similarly “to reduce” with a positive amount (e.g., “to lower by 1‰”, not “to lower by –1‰”).

Page 1, line 8: please add the reference for the standard ratio (Craig, 1957).

Page 2, line 17: please explain what a “free box atmosphere” is

Page 3, line 30: the correct units for temperature in the parametrization for ϵ are “K” not “°C” (try to apply it at 0°C. . .)

Page 5, line 11: strange sentence construction. I suggest to rephrase as “[. . .] we express $\delta^{13}\text{C}_{\text{bio}}$ as a percentage (denoted $\delta^{13}\text{C}_{\text{bio}}^{\text{perc}}$ because [. . .]”

Page 5, line 16: the absolute values are superfluous as both F_{up} and F_{down} are positive (cf. SI 1B, and also Heinze and Maier-Reimer (1999))

Page 5, line 18: F_{net} should be defined as $F_{\text{net}} = F_{\text{up}} - F_{\text{down}}$ (cf. SI 1B, and also Heinze and Maier-Reimer (1999))

Page 6, line 25: replace “results in room” by “leaves room”

Page 6, line 27: replace “times slower” by “times more slowly”

Page 7, line 11: “(Fig. S4 and 5)” should probably read “(Fig. S4 and S5)”

Page 7, line 17: the sentence “Slow gas exchange reduces $F_{\text{u+d}}$ causing less fractionation to occur. . .” does not really make sense. Fractionation is dependent on temperature, which remains unchanged. The *contrast* or the *difference* between air and sea is changed, because the air-sea-exchange fluxes play a lesser role in the surface ocean ^{13}C balance allowing a greater difference between atmosphere and ocean. Please rewrite.

Page 8, line 25: “can be”? is it or is it not? If it is, say “is”, else please discuss!

Page 9, line 2: replace “is more confined to” by “is confined closer to”

Page 9, line 27: “probably”? Why speculate? The model results should allow to verify this.

Page 10, line 11: replace “(up to -0.8‰)” by “(by up to 0.8‰)”

Page 11, line 5: “course” should read “source”

Page 11, line 6: replace “earlier” by “previously”

Page 11, line 10: Fig. S6 relates to the slow gas experiment. Not sure this is the one to refer to here.

Page 11, line 13: replace “with” by “by”

Page 11, line 27: replace “advance” by “spread” or “extend”

Page 11, line 28: replace “increased up to” by “increased by up to”

Page 12, line 1: replace “varies up to $\sim\pm 0.4\text{‰}$ ” by “varies by up to about $\pm 0.4\text{‰}$ ” (do not place two symbols immediately one after the other)

Page 13, line 19: replace “varies up to $\sim\pm 0.5\text{‰}$ ” by “varies by up to about $\pm 0.5\text{‰}$ ”

Page 13, line 21: “is important” should read “are important”

Supplementary Information

Page 2: there is much confusion and there are several errors in this paragraph. To bring it in line with the graphs, the model documentation (Heinze and Maier-Reimer, 1999) and the main paper, it needs to be corrected as follows:

- $F_{\text{up}} = k_w * [A]_{\text{water}}$
- $F_{\text{down}} = k_w * [A]_{\text{air}}$
- $F_A = k_w * ([A]_{\text{water}} - [A]_{\text{air}})$

Page 4, caption to Fig. S3: what exactly is meant by “Negative values indicate a potential carbon flux to the ocean?” Why “potential”?

Page 4, caption to Fig. S4: not sure what the integrated fluxes are meant to tell. Is there something special after 100 years? We try to understand the state after 2000 years. Why is the state after 2000 years not shown here instead?

Page 4, Figs. S3 and S4: unfortunately, the color scales chosen here are somewhat misleading. On Fig. S3, the rich green tone covers the first negative interval (i.e., the one next to 0) while on Fig. S4, it covers the first positive interval.

Page 5, Fig. S5: It would be best if all the figures had the same vertical axis extent. If this is not possible, at least graphs appearing side by side should have the same extents (both pCO_2 and $\delta^{13}\text{C}$ axes).

References

- Craig, H.: Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide, *Geochim. Cosmochim. Ac.*, 12, doi:10.1016/0016-7037(57)90024-8, 1957.
- Derry, L. A. and France-Lanord, C.: Neogene growth of the sedimentary organic carbon reservoir, *Paleoceanography*, 11, 267–275, doi:10.1029/95PA03839, 1996.
- Heinze, C. and Maier-Reimer, E.: The Hamburg Oceanic Carbon Cycle Circulation Model version “HAMOCC2s” for long time integrations, Technical Report 20, Deutsches Klimarechenzentrum, Hamburg (DE), available at <https://www.dkrz.de/mms/pdf/reports/ReportNo.20.pdf>, 1999.