Review of MS by Jun Shao et al.

Fortunat Joos

The paper forcefully demonstrates that air-sea gas exchange effectively acts to couple atmospheric and upper ocean d13C. This point is, - from a modelling point of view and for all those monitoring the penetration of the anthropogenic perturbation into the ocean - rather trivial and not new. The timescale to bring the surface layer in equilibrium with a d13C perturbation in the atmosphere by air-sea gas exchange is of order 10 years as outlined by Broecker, Peng and others. Numerous measurements of CFCs, bomb-produced radiocarbon, DIC, and notably of d13C demonstrate that the atmospheric perturbation in these tracers is communicated by air-sea gas exchange to the surface layer and by surface-to-deep exchange to deeper layers within years to decades (e.g., (Heimann and Maier-Reimer 1996;Broecker et al. 1985;Eide et al. 2017). Thus it is clear from an observational as well as from a modelling point that air-sea gas exchange is important and needs to be considered when addressing carbon isotopes. Unfortunately, the role of air-sea exchange is sometimes neglected in the interpretation of marine planktonic d13C records. It may therefore be appropriate to recall this point for the paleoceanographic tracer community.

We thank the reviewer for his very thorough and helpful review. We agree that the principle behind a dominant rule of air-sea gas exchange on surface δ^{13} C is quite well established in theory and is 'well known' in the modeling community (e.g. Schmittner et al., 2013). We are very happy to revise the manuscript to include these points and better highlight the coupling between ocean and atmosphere. However, in the specific hypotheses we address, the situation is subtly different – although eventually the signature of isotopically depleted carbon release must reach the atmosphere and hence be re-transmitted to the entire global surface ocean (via air-sea gas exchange), the question is whether the observed δ^{13} C decline in specific planktic and shallow/intermediate depth benthic records reflect the 'end point' (following ocean invasion of the signature globally from the atmosphere), or whether they reflect a location on the pathway of carbon release from the ocean (and hence prior to invasion to the atmosphere and global surface re-equilibrium). We admit this was not fully clear in the original text and will discuss the competing hypotheses (plus sequence of events, and the inevitable role of air-sea gas exchange) much more clear.

Interesting is that the authors offer a quantification of the influence of preformed versus remineralized changes in d13C. However, the method applied to separate changes in d13C into the contribution from preformed sources and sources from biogenic particles is unclear and may not be appropriate (see below).

In the cGENIE model the numerical tracer is exact by definition, but we agree that there are a number of caveats that we did not discuss when deriving regenerated δ^{13} C from other modelled metrics (as we do in LOVECLIM). We address this in response to the detailed Referee comments below.

Another interesting point, which deserves a bit more discussion, is the information on the change in d13C versus the change in atmospheric CO2 in response to an increase in deep ocean

ventilation (AABW, AAIW) forced by prescribed changes in salt and Southern Ocean wind stress.

I recommend major revisions. Specific comments:

1) Attribution of the d13C changes.

Section 2.3 The separation into preformed and remineralized d13C from the model output of DIC and d13C appears problematic. The assumption and simplifications of the approach are not explained to the readers

We will fully rectify this.

It would be preferable to simulate the preformed tracers online.

We do in cGENIE. But the historical/published nature of the LOVECLIM experiments means that we are unable to simulate the preformed tracers online for LOVECLIM (hence the use of cGENIE to elucidate the errors in the approximation we then must use).

1. a) The authors use the equations given in line 124 to estimate the change in δ 13C due to a change in remineralization. However, the equation is unclear. A new term is used in this equation: "12Corg". I guess 12Corg should read DICorg, the amount of remineralized carbon. Then the equation given by the authors reads:

 δ 13Cr=d13Corg * Δ (DICorg /DIC) (1)

We admit some sloppiness with the notation, which we will correct and much better clarify.

2. b) How is δ^{13} Corg computed? I get the impression that a constant δ^{13} C signature of organic carbon (δ^{13} Corg) is assumed in the approach applied to distinguish the preformed and remineralized components in LOVECLIM.

As per earlier comments (and also subsequent replies) – we will extensively revise the text to more logically and explicitly detail: the role of cGENIE vs. LOVECLIM, how the preformed tracers are simulated in cGENIE, how respired δ^{13} C is estimated in LOVECLIM and what the error (based on cGENIE analysis) are.

c) Any perturbation in surface δ^{13} C is also transferred to newly formed organic matter and CaCO3 and finally to remineralized carbon. In addition, changes in surface CO2 affect the fractionation factor for organic matter formation and thereby again d13Corg. Further changes in

surface d13C also affect changes in the signature of preformed fluxes. It appears that changes in the isotopic signature of preformed and remineralized carbon fluxes are neglected. This seems an oversimplification.

We agree, and it was an omission not to discuss this in the original manuscript. (We note that the cGENIE preformed tracer analysis encapsulates *all* errors, but these were not broken down as highlighted by the Referee.)

d) The equation on line 124 used to compute the change in remineralized δ 13C needs to be properly derived. The mass balance should be considered in the separation of the different components. I distinguish preformed DIC (DICp; index p) and remineralized DIC (DICr; index r) and related fluxes (Fp, Fr).

Changes in $\delta 13C$ can arise due to changes in the carbon fluxes, but also due to changes in the signature of the carbon fluxes.

Let us consider a single box of Volume V and inorganic C concentration DIC with an isotopic signature δ^{13} C. The fluxes of preformed DIC entering and leaving the box are denoted Fp,i, with i an index for the different fluxes covering all fluxes by diffusion, advection, and convection entering or leaving the box. Their signature is δ^{13} Cp,i. For simplicity, we consider one flux of remineralized carbon entering the box, Fr, with the signature δ^{13} Cr,in. Mass balance is then given by:

 $V * d/dt (DIC) = Sum(Fp,i) + Fr (2a) V * d/dt(DIC * \delta^{13}C) = Sum(Fp,i * \delta^{13}Cp,i) + Fr * \delta^{13}Cr,in (2b)$

Subtracting steady state fluxes and considering the change (Δ) over one time step of length Δt , we get with Δ (DIC) = $\Delta F/V * \Delta t$:

 $\Delta (DIC) = \Delta (DICp) + \Delta (DICr) (3a) \Delta (DIC * \delta 13C) = \Delta t/V * \Delta (Sum(Fp,i * \delta 13Cp,i) + \Delta (Fr*\delta 13Cr,in) (3b)$

Linearising (3b) and using again Δ (DIC) = Δ F/V * Δ t, we get: Δ (DIC) * δ 13C + DIC * Δ (δ 13C) = Δ (DICp) * δ 13Cp,in + Δ (DICr)* δ 13Cr,in

 Δ t/V *Sum(Fp,i * $\Delta(\delta 13$ Cp,i)) + Δ t/V * Fr * $\Delta(\delta 13$ Cr,in) (4)

The first two rhs terms in (4) describe the change in isotopic mass due to the addition of carbon by the perturbed preformed and remineralized carbon fluxes. The last two rhs terms describe the change due to the change in the signature of the preformed and remineralized carbon fluxes. Equations 4 has many unknowns ($\Delta(\delta 13Cr)$, $\Delta(\delta 13Cp)$, $\delta 13Cr$, in and $\delta 13Cp$, in ...). Thus, it seems not possible to attribute the change in $\delta 13C$ to preformed and remineralized components in an exact way without carrying a separate preformed d13C tracer in the model.

(Indeed, hence the inclusion of the new preformed $\delta^{13}C$ tracer in cGENIE.)

Perhaps it is justified to make approximations. We may assume that

 Δ (DICp) * δ 13Cp,in $\ll \Delta$ (DICr)* δ 13Cr,in. (5)

This is probably o.k. as $\delta 13$ Cp,in is close to zero permil and and d13Cr,in is about -20 permil for organic material.

It is much less clear whether also the terms with the changes in the isotopic signatures in eq. (4) can be neglected. The changes in δ 13C may be small, but they are multiplied with the total carbon fluxes (Fr, Fp,i) and not just with the perturbations in the carbon fluxes. Therefore, these terms may be very significant. Nevertheless, let us assume for the moment these two terms are negligible. In this case, we get:

 Δ (DIC) * δ 13C + DIC * Δ (δ 13C) ~ Δ (DICr)* δ 13Cr,in and the solution for Δ (δ 13Cr) is:

 Δ (δ 13Cr) ~ Δ (DICr)/DIC * (δ 13Cr,in – δ 13C) - Δ (DICp)/DIC * δ 13C (6)

Eq. 6 is somewhat similar to the eq. (1) above and given on line 124 in the MS, when setting δ 13Corg= δ 13Cr,in- δ 13C. This difference in isotopic signatures of the material remineralized and of the isotopic signature of DIC should be considered. In particular, in the upper ocean δ 13C of DIC is different from zero.

In addition, it seems that the parentheses are not properly set in (1) and eq. 1 should rather read $\delta 13$ Cr=d13Corg * Δ (DICorg) /DIC.

Further, the second rhs term of (6) is neglected in (1). The second rhs term in eq. 6 may be small as typical source signatures are between 0 and 2 permil in the upper ocean. However, it seems easy to account for in the evaluation of $\Delta(\delta 13 \text{Cr})$.

In conclusion, the calculation of the change in $\delta 13C$ attributable to organic matter remineralization and to preformed fluxes must be revised. It remains the task of the authors to demonstrate that changes in the isotopic signature of the preformed and remineralized fluxes can either be safely neglected (as done to get eq. (6) or otherwise to properly account for their influence.

We intend to address this via a full attribution analysis of the factors influencing $\delta^{13}C$ in the ocean. Using cGENIE, we will start by elucidating the error terms involved in making the step (employed in LOVECLIM): AOU \rightarrow regenerated PO₄, and in the context not only of preindustrial steady-state conditions, but under transient deglacial-like boundary condition changes. We will then do similarly (using cGENIE) for the step: regenerated PO₄ \rightarrow regenerated $\delta^{13}C$. To fully break down the error terms (as outlined above by the Refree), we will carry out a series of cGENIE experiments in which we: (a) we fix the ¹³C fractionation into organic matter (i.e. making it independent of changes in $[CO_{2(aq)}]$) and (b) run with and without fixed atmospheric composition. Together, we should be able to explicitly elucidate all the contributions to changing ocean $\delta^{13}C$ and hence in respect in reconstructing regenerated $\delta^{13}C$ from AOU in LOVECLIM, not only what the net error is (which we included in the submitted manuscript), where how large and from where the contributing terms arise. My recommendation is to explicitly include preformed tracers in LOVECLIM and then to repeat the simulation shown in figure 1 with the preformed tracers enabled in this model of intermediate complexity.

In an ideal world, yes. However, implementing new tracers in LOVECLIM and then repeating a previously published experiment is not practical and would require several months of work and run-time. We see our approach as analogous to the CMIP/PMIP series of model inter-comparison experiments, where published experiments are subsequently 'mined' and reanalyzed (and typically without re-coding and re-running). Our methodology is somewhat aligned with this workflow.

The simulations have been published before and the separation of d13C changes into preformed and remineralized components is the main point of this paper. Thus, this separation should be done properly to make this manuscript publishable.

Accepted. See above for the additional cGENIE modelling that we propose to fully elucidate the different sources of error involved in approximating regenerated δ^{13} C. The advantage of this approach over a single model run presenting only an explicit (numerical tracer) preformed δ^{13} C tracer based analysis is that it gives us the chance to evaluate how different processes control δ^{13} C distributions and changes in the ocean (as outlined by the Referee above) together with the uncertainties involved in published approaches of approximating based on AOU or preformed phosphate tracers.

As to the specific mass balance calculations, we will modify the relevant method section along the lines of:

"Our formulation is based on the following mass balance:

 $\delta^{13}C * DIC = \delta^{13}C_{pref} * DIC_{pref} + \delta^{13}C_{reg} * DIC_{reg}$ (1)

 $\delta^{13}C$ anomaly can be expressed as:

 $\Delta \delta^{13} C = \Delta (\delta^{13} C_{\text{pref}} * \text{DIC}_{\text{pref}} / \text{DIC}) + \Delta (\delta^{13} C_{\text{reg}} * \text{DIC}_{\text{reg}} / \text{DIC}) \quad (2)$

The first and second term on the RHS represents the $\delta^{13}C$ anomaly that due to changes in the preformed and regenerated component, respectively.

Since the regenerated component is dominated by organic carbon and there is no ¹³C fractionation during CaCO₃ formation in the model, the second term on the RHS ~ $\Delta(\delta^{13}C_{org} * DIC_{org} / DIC)$. We use AOU to estimate dissolved organic carbon and its contribution to the $\delta^{13}C$ anomaly: $\Delta(\delta^{13}C_{org} * DIC_{org} / DIC) = \Delta(\delta^{13}C_{org} * AOU * R_{c:-o2})$, where $\delta^{13}C_{org}$ is estimated by the global mean $\delta^{13}C$ of POC (~ -31‰) as simulated in LOVECLIM, $R_{c:-o2} = 117$:-170.

This leads to:

 $\Delta \delta^{13} C = \Delta (\delta^{13} C_{\text{pref}} * \text{DIC}_{\text{pref}} / \text{DIC}) + \Delta (\delta^{13} C_{\text{org}} * \text{AOU} * R_{\text{c:-o2}}) (3)$

The anomaly is defined as the difference between 15 and 17.2 ka, equation (3) thus expands as:

 $\delta^{13}C^{15ka} - \delta^{13}C^{17.2ka} = \delta^{13}C_{pref}^{15ka} * DIC_{pref}^{15ka} / DIC^{15ka} - \delta^{13}C_{pref}^{17.2ka} * DIC_{pref}^{17.2ka} / DIC^{17.2ka} + \delta^{13}C_{org}^{15ka} * AOU^{15ka} * R_{c:-o2} / DIC^{15ka} - \delta^{13}C_{org}^{17.2ka} * AOU^{17.2ka} * R_{c:-o2} / DIC^{17.2ka}$ (4)

It is well known that AOU likely overestimates the true oxygen utilization, and thus DIC_{org} , particularly in water masses formed in high latitudes (Bernardello et al., 2014; Ito et al., 2004; Khatiwala et al., 2019). However, to what extent these biases will affect the relative contribution of preformed and regenerated carbon pool on $\delta^{13}C$ anomaly in a carbon cycle perturbation event has never been evaluated. To validate the results we obtained from LOVECLIM, we conducted a benchmark test with another Earth System model – cGENIE."

2) Line 149-158: The authors separate surface ocean δ 13C change into a thermodynamic equilibrium component and a residual component. I am puzzled by the interpretation offered by the authors. The authors state that the residual component mainly reflects changes in primary productivity. This is not demonstrated but only inferred from simulated changes in productivity. The balance between the input of PO4 by upwelling and consumption of PO4 by export leads to a positive PO4 anomaly in the SO surface ocean (Fig 3d). Correspondingly, the balance of upwelling and export alone leads to a negative δ 13C anomaly in the SO ocean surface. It is unclear to which extent incomplete air-sea exchange contributes to this residual component.

It's true that in the model, even though the surface productivity increased, the overall efficiency of the biological pump decreases when deep ocean overturning rate increases. It's also true that incomplete air-sea exchange is somewhat ignored in this separation. To focus on the main point of this paper, we will remove this part in the revision. With hindsight, this decomposition was one step in δ^{13} C attribution too far and wholly unnecessary (and confusing as also remarked upon by Referee #1).

3) The LOVECLIM simulation is forced by prescribed changes in wind stress and salt fluxes (Fig. 1a,b). This triggers a change in Southern Ocean upwelling and deep ocean ventilation (as e.g., reflected by AABW changes in Fig. 1c). One may then ask which part of the early deglacial CO2 rise may be explained by such a change in deep ocean ventilation.

The ratio between the change in atmospheric $\delta 13C$ and CO2 interesting as this ratio can be directly compared with ice core data as done in previous work.

The change in deep ocean ventilation and Southern Ocean upwelling enforced by prescribed wind stress and freshwater forcing causes δ 13C to decline by 0.35 and CO2 to increase by 25 ppm in the LOVECLIM simulation (Fig 1c). This yields a ratio of 7 ppm per 0.1 permil decline. (Tschumi et al. 2011) performed similar idealized simulations where Southern Ocean overturning was changed by prescribed changes in boundary conditions. They found a ratio of 13 ppm per 0.1 permil decline. The ice core data suggest an increase in CO2 of 35 ppm and a decrease in d13C of 0.3 permil during the early deglacial period. This corresponds to a ratio of 12 ppm per 0.1 permil decline. Tschumi et al. suggested that the entire increase in CO2 of 35 ppm during the early deglacial was due to enhanced Southern Ocean upwelling. The

LOVECLIM results suggest a smaller contribution of SO upwelling to the early deglacial CO2 rise. According to LOVECLIM only 25 ppm of the deglacial CO2 rise are attributable to the prominent Southern Ocean upwelling hypothesis.

This issue should be discussed in section 4.

The different $\Delta pCO_2/\Delta \delta^{13}CO_2$ sensitivity the reviewer is referring to can be mainly explained by different initial conditions in the two studies - Tschumi et al., 2011 applied pre-industrial conditions while the transient LOVECLIM simulation analyzed in this study started from a LGM state, that was benchmarked against benthic $\delta^{13}C$ data. Deep ocean $\delta^{13}C$ is ~0.6‰ lighter at the LGM than the Holocene (Peterson et al., 2014). Therefore, for the same magnitude of atmospheric pCO₂ increase through enhanced SO upwelling, $\delta^{13}CO_2$ decline in LOVECLIM is larger. Appropriate initial conditions are necessary to investigate the carbon cycle perturbation that led to a negative excursion in $\delta^{13}CO_2$ during the early deglaciation.

Menviel et al. 2015 present the atmospheric pCO₂, δ^{13} CO₂ and oceanic d13C responses to changes in oceanic circulation in LOVECLIM and the Bern3D under pre-industrial conditions. As seen in their figure 4, for changes in Southern Ocean buoyancy forcings, $\Delta pCO_2/\Delta \delta^{13}CO_2$ ratio is +16ppm per 0.1‰ decline in LOVECLIM and +8.3ppm per 0.1‰ decline in Bern3D; for changes in SH westerlies, $\Delta pCO_2/\Delta \delta^{13}CO_2$ ratio is +10ppm per 0.1‰ decline in LOVECLIM.

As noted by the reviewer (and unfortunately not included in Menviel, et al. 2015), changes in SH westerlies lead to a 12 ppm CO₂ increase for a $0.1\% \delta^{13}CO_2$ decrease in the Bern3D as per Tschumi et al., 2011. The (slight) difference in sensitivity between the models could come from differences in the initial oceanic $\delta^{13}C$ distributions with a negative $\delta^{13}C$ bias in the equatorial regions at intermediate depth in LOVECLIM (see figure 3 of Menviel et al., 2015).

We think changes in atmospheric pCO2 and $\delta^{13}CO_2$ during the early part of the deglaciation represent the integrated signal of different processes: a significant AMOC weakening, an increase in SO ventilation, a decrease in SO sea-ice cover, an increase in globally averaged SST, and changes in the terrestrial biosphere. While idealized simulations of changes in SH westerlies provide information on the probable $\Delta pCO_2/\Delta \delta^{13}CO_2$ change, the actual integrated response is more complex.

Although this topic is of interest, it is more related to published work rather than the main point of this paper - $\delta^{13}CO_2$ decline during the early deglaciation can account for most of the marine planktic and shallow/intermediate benthic $\delta^{13}C$ decline in the global ocean. Thus we will add some elements of the above discussions to the Introduction rather than adding a new discussion section.

Minor comments:

Intro: It is suggested to change the framing of the introduction. It should be clearly pointed out that it is very well established by the modelling community and by those addressing the anthropogenic carbon perturbation that air-sea gas exchange influences d13C, but that this well-established fact is sometimes neglected in interpretation of planktonic d13C records. It would be

appropriate to recall the typical equilibration time of 10 yr for d13C in the surface layer by airsea gas exchange and the typical decadal timescale of surface-to-thermocline transport as revealed by observations of anthropogenic tracers.

We are happy to make appropriate changes to the Introduction as part of framing the competing hypotheses more clearly and the role of ocean surface / atmosphere equilibrium.

The revised text has been provided in our response to the reviewer's major comments above.

L51-52: I do not understand the conclusion that atmospheric CO2 is not affected. If atmospheric CO2 (and d13C) varies/is perturbed, e.g., by outgassing in the Southern Ocean, then the CO2 perturbation will like the d13C perturbation enter the upper ocean.

The relevant text will be changed along the lines of:

"The 'top down' and 'bottom up' scenarios have different implications: In the 'bottom up' transport scenario, δ^{13} C anomaly in the marine planktic and upper intermediate depth benthic records can be used as evidence of enhanced flux of ¹³C-depleted carbon from the deep ocean, while in the 'top down' scenario, such an inference is invalid."

L57: This is a somewhat odd description of the preformed component. The preformed component reflects the balance between all tracer sources and sinks in a surface grid cell. Upwelling and exchange with the deeper layers are generally equally important as air-sea exchange and export production. Why highlighting the terms thermodynamic equilibrium and primary productivity? Would it not be more appropriate to mention air-sea gas exchange and new or export production as well as physical tracer exchange between surface and deeper layers?

This part will be removed (and as per our reply above).

L109: "The atmosphere is held constant ..allowed to evolve freely" This text is unclear. Do you mean in the experiment "fix" atm. CO2 and d13C is kept constant and in exp. "free" CO2 and d13C evolve freely?

Yes exactly. We will better clarify this in revision.

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