Authors'response to the comments of the first reviewer

We would like to express our sincere gratitude to the reviewer for the careful evaluation of our manuscript and for the insightful comments and suggestions. The reviewer's comments are reproduced below in italics, followed by our responses. All modifications introduced in the revised manuscript are indicated in bold burgundy text.

Major comments

1. "Equations (2), (5), and (8): If I understand the derivation correctly, a factor of 2 may be missing before the isotope ratio term (R) in Eqs. (2), (5), and (8). The conversion between isotopologue abundances and bulk isotope ratios for O_2 requires a factor of 2 arising from the symmetry of the O_2 molecule (Yeung et al., 2012). Although this omission may have only a minor impact on the numerical results if implemented consistently throughout the model, the equations should be verified and clarified to ensure that the formulation is physically and chemically correct."

Response: We thank the reviewer for pointing out this important aspect. The reviewer is correct that, when converting between O_2 isotopologue abundances and atomic isotope ratios, a factor of 2 arises because the singly substituted isotopologues can occur in two symmetry-equivalent molecular arrangements (e.g., Yeung et al., 2012). The reviewer identified an ambiguity in our notation.

In our model, the simulated tracers correspond to the bulk abundances of the isotopologues, such that $^{33}O_2 = {}^{16}O^{17}O + {}^{17}O^{16}O$ and $^{34}O_2 = {}^{16}O^{18}O + {}^{18}O^{16}O$. Doubly substituted isotopologues (e.g., $^{17}O^{17}O$) are not represented because of their negligible abundance. The isotope ratios (^{17}R and ^{18}R) used in Eqs. (2), (5), and (8) are then calculated as atomic isotope ratios from these bulk isotopologue abundances. Consequently, the factor of 2 is introduced identically in both the sample and the isotopic standard and therefore cancels during isotope-ratio normalization:

$$\delta^{18}\text{O–}O_2 = \left(\frac{2 \times {}^{18}R}{2 \times {}^{18}R_{\text{std}}} - 1\right) \times 1000 = \left(\frac{{}^{18}R}{{}^{18}R_{\text{std}}} - 1\right) \times 1000 \quad (1)$$

The same reasoning applies to δ^{17}O-O_2, and consequently the calculated $^{17}\Delta_{\text{ocean}}$ is also unchanged.

We agree that the previous notation could be interpreted as implying that the two symmetry-equivalent molecular arrangements were explicitly represented. To remove this ambiguity, we have revised the text to clarify that $^{33}O_2$ and $^{34}O_2$ denote the bulk abundances of the singly substituted isotopologues. We also verified that introducing the factor of 2 consistently in both the sample and reference isotopologue abundances leaves the calculated δ^{18}O-O_2 and $^{17}\Delta_{\text{ocean}}$ unchanged because the factor cancels during isotope-ratio normalization.

Revised version: To avoid confusion between atomic isotope ratios and O_2 isotopologue abundances, the manuscript has been revised as follows:

- **Lines 27-28** The definition of the isotope ratio has been clarified : "Isotopic ratio *R (* = 17 or 18) is computed as the abundance ratio of the heavy oxygen isotope (^{17}O or ^{18}O) relative to the most abundant oxygen isotope (^{16}O)."
- **Lines 143-146** The description of the tracer implementation has been revised: "To simulate $^{17}\Delta_{\text{ocean}}$, three tracers corresponding to the bulk abundances of $^{32}O_2$, $^{33}O_2$ and $^{34}O_2$

are incorporated into iLOVECLIM through the previously described processes (Fig. 1). The $^{33}O_2$ and $^{34}O_2$ tracers correspond to the bulk abundances of the singly substituted isotopologues (i.e., $^{16}O^{17}O + {}^{17}O^{16}O$ and $^{16}O^{18}O + {}^{18}O^{16}O$, respectively), without explicitly distinguishing between the two symmetry-equivalent molecular arrangements."

- **Lines 181-182** For consistency, we also revised the description of isotopic fractionation to refer to oxygen isotopes rather than oxygen isotopologues: "Furthermore, isotopic fractionation factors associated with oxygen isotope fractionation are prescribed as constants."

2. "Sensitivity tests of key parameters: The model evaluation relies on a number of prescribed parameters, including the coefficient of 2 in Eq. (10), the respiration fractionation factors ($^{18}\alpha_{respiration} = 0.980$ and $^{17/18}\theta_{respiration} = 0.518$), the atmospheric $^{17}\Delta O_2$ boundary condition, and the initial dissolved O_2 concentrations and isotope compositions. Several of these parameters remain incompletely constrained and may exert a first-order control on the simulated distributions of $\delta^{18}O$–O_2 and $^{17}\Delta_{ocean}$. Moreover, the manuscript repeatedly suggests that some of the model–data discrepancies, particularly the overestimation of $^{17}\Delta_{ocean}$ in deep waters and the Southern Ocean, may result from the choice of respiration fractionation parameters. However, this hypothesis is not evaluated quantitatively. Given that the implementation of oxygen isotopes is the primary development presented in this study, the manuscript would be substantially strengthened by including sensitivity experiments that explore plausible ranges of the key isotope parameters. Such analyses would help determine whether the remaining model–data mismatches primarily reflect parameter uncertainty or structural limitations of the model itself, while also providing a useful assessment of the robustness of the simulated isotope fields."

Response: We thank the reviewer for this thoughtful and constructive comment. We fully agree that isotopic fractionation factors and atmospheric boundary conditions can influence the simulated distributions of $\delta^{18}O$–O_2 and $^{17}\Delta_{ocean}$. Likewise, the initial isotopic composition may affect the transient adjustment of the simulations, although its influence becomes negligible once isotopic equilibrium has been reached following the multi-millennial spin-up performed in this study.

We also agree that sensitivity analyses are essential for quantifying parameter uncertainty and distinguishing it from structural model limitations. However, the primary objective of the present manuscript is to describe the implementation of the triple oxygen isotope framework within iLOVECLIM and to evaluate its ability to reproduce the observed large-scale distributions of $\delta^{18}O$–O_2 and $^{17}\Delta_{ocean}$. That falls within the scope of a model development paper in GMD, which focuses on documenting new model developments, verifying their correct implementation, and evaluating their performance against available observations. Accordingly, isotopic fractionation factors, atmospheric boundary conditions, and initial isotope compositions were prescribed using values commonly adopted in the literature and treated as fixed inputs throughout this study.

We acknowledge that the remaining model–data mismatches, particularly the overestimation of $^{17}\Delta_{ocean}$ in the Southern Ocean and in some deep-water regions, may partly result from uncertainties in these prescribed parameters. A systematic exploration of the associated parameter space would therefore be highly valuable. However, such an analysis requires a large ensemble of equilibrium simulations and falls beyond the scope of the present implementation and evaluation study. To address this question, the sensitivity of simulated $\delta^{18}O$–O_2 and $^{17}\Delta_{ocean}$ to biological isotopic fractionation parameters is investigated in a dedicated follow-up study (Clermont et al., submitted to JGR: Oceans, doi: 10.31223/X5BF68). This study uses a 300-member ensemble

generated through a Latin Hypercube Sampling approach and demonstrates that isotopic fractionation parameters exert a control on the simulated isotope fields. The analysis also identifies parameter combinations that improve agreement with available observations. The influence of other prescribed parameters, including atmospheric boundary conditions, remains to be investigated in future work.

Nevertheless, we fully agree with the importance of this question. We therefore added a statement in the manuscript highlithing this limitation.

Revised version: The following sentence has been added to the Conclusion section: "In addition, uncertainties associated with isotopic fractionation factors and atmospheric boundary conditions may contribute to the remaining discrepancies between simulations and observations. Future sensitivity analyses will help quantify their influence on simulated δ^{18}O–O_2 and $^{17}\Delta$ocean, and distinguish parameter uncertainty from model structural limitations."

3. "Air–sea gas-exchange isotope fractionation: The manuscript does not explicitly state the oxygen isotope fractionation factors used for air–sea gas exchange. Because air–sea exchange is one of the three fundamental processes controlling $^{17}\Delta_{\mathrm{ocean}}$, these values should be clearly documented. In addition, experimental studies have demonstrated that both kinetic and equilibrium isotope fractionation during O_2 gas transfer can substantially influence dissolved O_2 isotopologue compositions and, consequently, gross primary productivity estimates derived from $^{17}\Delta_{\mathrm{ocean}}$ (Li et al., 2019). This effect may be particularly important in low-productivity regions where the biological signal is relatively weak. I therefore recommend that the authors explicitly report the fractionation parameters used in the model and discuss their potential influence on the simulated isotope fields."

Response: We thank the reviewer for this helpful and constructive comment. We fully agree that isotope fractionation during air–sea gas exchange is one of the fundamental processes controlling the isotopic composition of dissolved oxygen and should be clearly documented. Accordingly, we have revised the manuscript to explicitly report the equilibrium and kinetic isotope fractionation factors adopted in the model together with their corresponding references.

Following the reviewer's suggestion, we further investigated the influence of these fractionation factors by performing an additional sensitivity experiment using the updated air–sea gas-exchange isotope fractionation parameters reported by Li et al. (2019). Rather than simply reporting the adopted values, we considered it useful to evaluate how these updated experimental constraints affect the simulated distributions of δ^{18}O–O2 and $^{17}\Delta$ocean. To present these new results, we have added a new discussion section in the manuscript (Section 4.3), where we compare the reference simulation with the simulation using the updated fractionation factors. The sensitivity experiment shows that the revised parameterization produces relatively small regional changes in δ^{18}O–O2, whereas its influence on $^{17}\Delta$ocean is more pronounced, particularly within oxygen minimum zones and the Southern Ocean. The updated fractionation factors reduce the model bias in these regions, especially within oxygen minimum zones. However, they do not fully resolve the remaining model–data discrepancies, as the revised fractionations does not significantly improve the overall agreement between the model and the observations at the global scale.

Overall, these additional simulations demonstrate that the updated air–sea gas-exchange isotope fractionation parameterization significantly influences the simulated isotope fields at the

regional scale, but is insufficient to explain the remaining large-scale discrepancies between simulations and observations.

Revised version: The equilibrium and kinetic isotope fractionation factors used for air-sea gas exchange are now explicitly reported in Section 2.2.2: "Furthermore, isotopic fractionation factors associated with oxygen isotopes are prescribed as constants. For air-sea gas exchange, the equilibrium fractionation factor for ^{18}O ($^{18}\alpha_{eq}$) is taken from Benson and Krause (1980, 1984), the kinetic fractionation factor ($^{18}\alpha_{k} = 0.9972$) from Knox et al. (1992), and the corresponding ^{17}O fractionation factors ($^{17}\alpha_{eq}$ and $^{17}\alpha_{k}$) from Nicholson et al. (2012)". According to the new section describe after, we also modified this sentence in the conclusion:"To improve the spatial distribution and magnitude of $^{17}\Delta_{ocean}$, further refinement of primary production schemes and vertical mixing processes is needed, particularly in the Southern Ocean, where adopting the updated air–sea gas-exchange isotope fractionation factors of Li et al. (2019) improves the simulated isotope fields but does not fully resolve the remaining model–data discrepancies, indicating that additional physical and biogeochemical processes are likely involved.". And, this new section 4.3 is added to the discussion:

4.3. Isotope fractionations during air-sea exchange

Air–sea gas exchange is one of the three fundamental processes controlling the isotopic composition of dissolved oxygen. The reference simulation (CTRL) uses the equilibrium and kinetic isotope fractionation factors described in Section 2.2.2. To evaluate the sensitivity of the isotopic tracers to recently revised air–sea isotope fractionation factors, we performed an additional simulation, hereafter referred to as the Exchange experiment, using the parameterization of Li et al. (2019). The corresponding fractionation factors are summarized in Table 1. Compared with the CTRL simulation, the equilibrium fractionation factor for ^{18}O remains unchanged, whereas the kinetic fractionation factor for ^{18}O and both the equilibrium and kinetic fractionation factors for ^{17}O are updated.

Table 1: Equilibrium and kinetic isotope fractionation factors that differ between the reference simulation (CTRL) and the simulation using the updated air–sea gas-exchange parameterization of Li et al. (Exchange).

	CTRL	Exchange
$^{18}\alpha_{eq}$	0.9972 [1]	0.9978 [2]
$^{17/18}\theta_{eq}$	0.518 [3]	0.528 [4]
$^{17/18}\theta_{k}$	0.518 [3]	0.517 [2]

Note: [1] Knox et al., 1992; [2] Li et al., 2019, [3] Nicholson et al., 2012, [4] Reuer et al., 2007 and Palevsky et al., 2016.

Figure 1 shows the differences in simulated $\delta^{18}O$–O_2 between the simulation using the updated air–sea exchange fractionation factors and the reference simulation (Exchange−CTRL). The impact of the revised parameterization on simulated $\delta^{18}O$–O_2 remains relatively small at the ocean surface (Fig. 1a), with anomalies generally ranging between -0.5 and 0.5 ‰. Surface waters exhibit slightly higher $\delta^{18}O$–O_2 values in the Exchange simulation, except in the Southern Ocean where lower values are observed. These negative anomalies propagate into the ocean interior, leading to decreases of up to 2.5 ‰ within oxygen minimum zones (Figs. 1b,c).

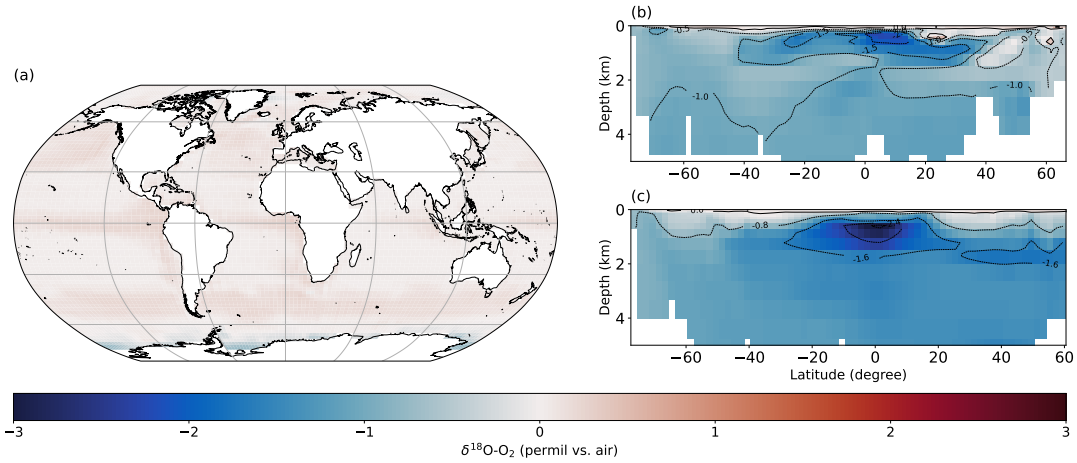

Figure 1: Differences in simulated δ^{18}O–O_2 between the simulation using the equilibrium and kinetic isotope fractionation factors from Li et al. (2019) and the reference simulation (Exchange−CTRL). (a) Surface ocean. (b) N-S cross-section of the central Atlantic Ocean. (c) N-S cross-section of the central Pacific Ocean

The impact is more pronounced for $^{17}\Delta_{\text{ocean}}$ (Fig. 2). At the ocean surface, differences range from approximately -10 to 10 ppm, with depleted values in the mid-to-high latitudes and equatorial regions, while enhanced values occur in the subtropical gyres (Fig. 2a). This spatial pattern highlights the regional influence of air–sea gas exchange on the isotopic composition of dissolved oxygen, especially in the regions of relatively weak biological productivity (e.g., subtropical gyres) or intense air-sea gas exchange (e.g., Southern Ocean). In the ocean interior, $^{17}\Delta_{\text{ocean}}$ in the Exchange simulation decreases by up to approximately 16 ppm, with maximum differences reaching -24 ppm within oxygen minimum zones (Figs. 2b,c). These pronounced anomalies indicate that changes in the isotopic signature acquired during air–sea gas exchange are subsequently transported into the ocean interior, where they amplify the differences between the two simulations.

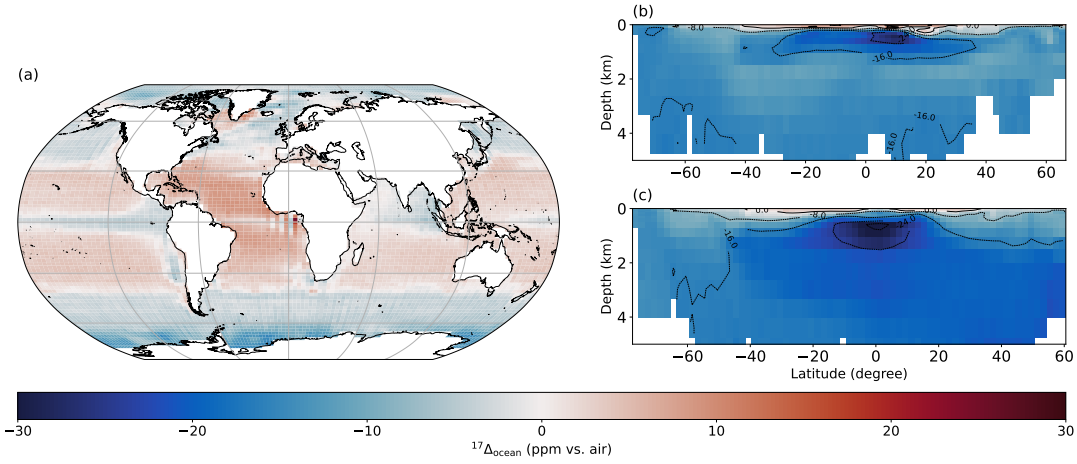

Figure 2: Differences in simulated $^{17}\Delta_{\text{ocean}}$ between the simulation uusing the equilibrium and kinetic isotope fractionation factors from Li et al. (2019) and the reference simulation (Exchange−CTRL). (a) Surface ocean. (b) N-S cross-section of the central Atlantic Ocean. (c) N-S cross-section of the central Pacific Ocean.

These changes are consistent with the experimental results of Li et al. (2019), confirming that the revised air–sea gas-exchange isotope fractionation factors exert a non-negligible influence on the isotopic composition of dissolved O_2. Despite these regional differences, the overall agreement between simulations and observations changes only marginally. The coefficient of determination remains unchanged for δ^{18}O–O2 ($R^2 = 0.70$ for both simulations), while it increases slightly for $^{17}\Delta$ocean, from $R^2 = 0.02$ in CTRL to $R^2 = 0.03$ in the Exchange simulation. These relatively low coefficients mainly reflect the comparison of climatological model fields with sparse observations collected over different seasons, years, and spatial scales, rather than a point-by-point evaluation.

Nevertheless, the updated coefficients noticeably improves the simulated isotope fields in oxygen minimum zones and in the Southern Ocean. Within oxygen minimum zones, the revised fractionation factors reduce δ^{18}O–O2 by up to 2.5 ‰ and $^{17}\Delta$ocean by up to 24 ppm, thereby reducing the model bias relative to the limited observations available in these regions (Fig. 12). Similar improvements are found in the Southern Ocean, although significant discrepancies remain. These results suggest that the revised air–sea gas-exchange fractionation factors improve the regional distribution of the simulated isotope fields but cannot, by themselves, explain the remaining Southern Ocean model–data discrepancies. Additional physical and biogeochemical processes are therefore likely to contribute to the persistent biases.

Minor comments

1, "In Eq. (7), should the asterisks on Osurf and Oeq be removed? Please verify the notation."
Revised version: The reviewer is correct. The unnecessary asterisks have been removed from O_{surf} and O_{eq} in Eq. (7).

2, "Line 184: "the the model" contains a duplicated word."
Revised version: The duplicated word has been removed.

3, "Table 1 uses inconsistent formats for reporting parameter uncertainty. Some entries are presented as ranges (e.g., [0.982–0.990]), whereas others are reported as mean ± uncertainty (e.g., 0.980 ± 0.003). Consider adopting a consistent format throughout the table."

Response: We thank the reviewer for this comment. The two formats were intentionally used to represent different types of information. Values reported as $x \pm y$ correspond to a reported mean with the measure of variability or uncertainty provided in the original study. In contrast, values presented as ranges indicate the full interval of values reported in the literature or observed across different environments. To avoid ambiguity, we have clarified the meaning of both notations in the table caption.

Revised version: The table caption has been revised to clarify that values reported as mean ± uncertainty correspond to central estimates with their associated uncertainty, whereas values reported as ranges represent the full interval of values reported in the literature.

4, "In Table 2, the simulated global $GPPO_2$ value (9.68×10^{15} mol O_2 yr^{-1}) is compared with estimates from Huang et al. (2021). However, the Huang et al. estimates represent the modern ocean, whereas the model is run under pre-industrial boundary conditions. Although the difference in global productivity between these two states may be modest, this mismatch should be acknowledged. The same caveat applies to the comparison of isotope tracers with modern observational datasets."

Response: We thank the reviewer for this important remark. We agree that the comparison between simulations performed under pre-industrial boundary conditions and observational estimates representative of the modern ocean should be interpreted with caution. In our model configuration, the main difference between pre-industrial and modern boundary conditions is expected to arise from atmospheric CO_2, which primarily affects climate and ocean temperature. However, CO_2 does not directly enter the oxygen cycle formulation implemented in the model. Its influence is indirect, through climate-driven changes in ocean conditions. Phytoplankton growth depends on temperature and light (Six and Maier-Reimer, 1996), so changes in atmospheric CO_2 may affect productivity through their effect on ocean temperature. Nevertheless, the global mean sea-surface temperature increase since the pre-industrial period is only on the order of 1 °C, suggesting that the resulting bias is likely smaller than other sources of uncertainty in the model formulation and observations.

Our objective in these comparisons is not to assess the model's ability to reproduce the exact modern state of the ocean, but rather to evaluate whether the implemented isotope framework produces realistic large-scale distributions and magnitudes consistent with available observations. Nevertheless, we agree that the mismatch

between pre-industrial simulations and modern observational estimates represents an additional source of uncertainty. We have therefore revised the manuscript to explicitly acknowledge this limitation when comparing model results with modern productivity estimates and isotope observations.

Revised version: The following sentence has been added in Section 2.3: "It should be noted that the observational datasets used in this study were collected under modern oceanic conditions, whereas the simulations were performed under pre-industrial forcing. Therefore, the comparison is intended to evaluate the large-scale consistency of the simulated oxygen and isotope distributions." In addition, the following sentence has been added to the section 3.2: "The simulation was performed under pre-industrial boundary conditions, whereas the estimates of (Huang et al., 2021) are representative of the modern ocean. Therefore, the following comparison focuses on the large-scale patterns and order of magnitude of simulated productivity. Compared with [...]". The caption of the Table 2 is also precised.

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