Manuscript: egusphere-2025-3649
Title: Advancing Isotope-Enabled Model for Comprehensive Understanding of Atmospheric Sulfur Isotope Effects: Demonstrating the Overlooked Isotopic Fractionation During Combustion and Flue Gas Desulfurization

We sincerely thank both reviewers for their thorough and constructive comments, which have significantly helped us improve the manuscript. Below we provide point-by-point responses to all comments. The reviewer's original comments are shown in black, and our responses are shown in blue. We have carefully considered each suggestion and will make corresponding revisions to the manuscript. Detailed responses for each comment are provided below. We look forward to submitting the revised manuscript for further consideration.

Responses to Reviewer 2 (RC2)

Reviewer's Overall Comment:

This paper presents a new isotope-enabled atmospheric chemistry model that simulates sulfur isotope fractionation during SO_2 oxidation and sulfate formation. The model tracks sulfur isotopologues through emissions, transport, chemistry, and deposition, while reducing biases associated with classical Rayleigh isotope calculations. It successfully reproduces observed sulfur isotope patterns over eastern China and shows that both atmospheric oxidation and combustion/desulfurization processes strongly influence sulfur isotopic signatures and source apportionment.

The scope of the paper is interesting and the proposed model is globally coherent with experimental data. The notations and mathematical derivations ought to be clarified, as detailed below, and the influence of the numerical scheme investigated further. Also, formulating the time-dependent evolution law for the fractionation dynamics would give a clear vue of the production/reservoir evolution, associated with the proposed in-depth discussion.

Author's Response: We thank the reviewer for their positive assessment of the scope and general coherence of the work. We are encouraged that the reviewer recognizes the value of the isotope-enabled modeling framework and its potential contributions to understanding atmospheric sulfur isotope effects. Below we address each in detail.

Comment 1 (Page 6)

Reviewer's Comment: Check notation between alpha as defined by Eq. 2 and the first alpha in Eq. 6.

Author's Response: Thank you. We have checked and unified the notation consistency between α as defined in Eq. 2 and the first α appearing in Eq. 6 as $\alpha^{{}^{h}x_{P/S}}$ to ensure the symbol meaning remains unchanged throughout the derivation.

Comment 2 (Page 6)

Reviewer's Comment: Precise how the average isotope ratio of accumulated product is calculated to obtain Eq. 7.

Author's Response: Thank you for this suggestion.

In the revised manuscript, we have clarified that Eq. 7 is the standard Rayleigh-fractionation expression for the average isotope ratio of the accumulated product, rather than a new derivation introduced in this study. We now cite (Hoefs, 2015) as the reference.

Comment 3 (Page 6)

Reviewer's Comment: Different notations are used in Eq. 9–10. We should have $\bar{R}$ and $\bar{R}$p in Eq. 9. Detail Eq. 10 and the simplifying approximation. What would be its magnitude?

Author's Response: We thank the reviewer for this careful observation.

(1) We have corrected the notation in Eq. 9 to be consistent with the rest of the manuscript. The revised equation is:

$$\overline{R_P} = R_{S,t0} \times \frac{1-f_{rem}^{(\alpha^{{}^{h}x_{P/S}}-1)}}{1-f_{rem}} \quad (9)$$

(2) Eq. 10 was an approximate expression of Eq. (9) in δ-notation, obtained by expanding the exponential term $f_{rem}^{(\alpha^{{}^{h}x_{P/S}}-1)}$ to first order in ε. The approximation error depends on the magnitude of ε and the remaining fraction f and is on the order of 0.1‰–0.5‰ under typical conditions, reaching up to ~1‰ at high conversion fractions. However, Eq. 10 is not used in our isotopic chemistry module, which directly computes isotope ratios from Eq. 9. We have therefore removed Eq. 10 from the revised manuscript to avoid unnecessary complexity.

Comment 4 (Figure 2)

Reviewer's Comment: New variables are introduced in the "solver" section of Fig. 2 that should be consistent with those in the text. The text in this section is too small and should be of readable size.

Author's Response: We thank the reviewer for this comment.

(1) We have also revised the variables in the solver section to match the notation defined in the main text and Text S2—specifically, the four isotopologues (${}^{32}SO_2$, ${}^{34}SO_2$, ${}^{32}SO_4^{2-}$, ${}^{34}SO_4^{2-}$), the isotope fractionation factor ($\alpha_{P/S}$), the reactant isotope ratio (R_S), and the product isotope ratio (R_P).

(2) We have also revised the corresponding body text in Section 2.4.2 to clearly describe the coupling between the host CTM and the isotopic chemistry module, the iterative calculation workflow, and the isotopologues tracking and update procedure.

Comment 5 (Page 10, Line 285)

Reviewer's Comment: "it assumes that a system that only" → "it assumes a system that only".
"When the Rayleigh equation is employed in the isotopic chemistry module": it is unclear how this equation can be optional? Shouldn't it be used to provide the fractionation information? How "fresh mixture" is included?
"The residual fraction of reactants frem, which is influenced by the time discretization": the model output should be robust to variations on the numerical scheme.
"Iterative time-splitting method": please provide a reference.

Author's Response: We thank the reviewer for these careful comments, which have helped us improve the clarity of Section 2.4.2.

(1) We have corrected the grammar.

(2) The Rayleigh equation is the core tool for calculating isotope fractionation and is not optional. Regarding how fresh mixture is included: within each main model time step, the total fresh SO_2 supplied by emissions, advection, and mixing is apportioned across the sub-steps of the iterative time-splitting method. At the start of each sub-step, the reactant concentration and isotope ratio are updated by incorporating the fresh reactant allocated to that sub-step, after which the Rayleigh-fractionation calculation is applied. This incremental procedure ensures that isotope fractionation is calculated in the presence of continuous fresh input, rather than over the full model time step where the closed-reservoir assumptions of the Rayleigh equation no longer hold. The revised Section 2.4.2 now describes this procedure in detail.

(3) We agree that model output should be robust to numerical discretization. The reason f_{rem} is influenced by time discretization is that the amount of SO_2 consumed within a time step depends on the reaction rate and the step length, so f_{rem} itself is time-step-dependent. When the Rayleigh equation is applied over a long time step, this discretization effect is amplified under larger SO_2 conversion fractions conditions. This provides the numerical motivation for the iterative time-splitting method, which confines each Rayleigh-based calculation to a small conversion sub-step. As demonstrated in Section 3.1, when the sub-step conversion threshold is reduced to 2%, the simulated isotope results converge and are insensitive to further refinement, confirming that the method achieves numerical robustness.

(4) The iterative time-splitting method was developed for this isotope-enabled CTM framework. The method is described in detail in Section 2.4.2, and its numerical validation and sensitivity tests are presented in Section 3.1 and Text S3.

Comment 6 (Page 11)

Reviewer's Comment: The relationship "$\alpha>1/\alpha<1$" is not mathematically correct. Do you mean $\alpha>1$?
"accumulated produce" → "accumulated product"

Author's Response: Thank you.

(1) The expression "$\alpha>1/\alpha<1$" is indeed mathematically incorrect. The original text mistakenly combined two separate conditions with a slash. In the revised manuscript, we have corrected this sentence to:

"The isotopic fractionation factor determines the direction of fractionation: when $\alpha > 1$, heavy isotopes are preferentially enriched in the product and depleted in the residual reservoir; conversely, when $\alpha < 1$, heavy isotopes are preferentially depleted in the product and enriched in the residual reservoir."

(2) We have changed "accumulated produce" to "accumulated product."

Comment 7 (Page 12)

Reviewer's Comment: "(see Text S3). Figure S1" → "(see Text S3), Figure S1"

"To mitigate the significant bias in simulated isotopic composition introduced by the Rayleigh equation in the isotopic chemistry module, we implement an iterative time-splitting method." If the Rayleigh equation is the source of a bias, it means that it's not adequate or it is misused; this shouldn't be solved by adjusting the numerical scheme.

Author's Response: We thank the reviewer for this insightful comment.

(1) We have corrected the punctuation error.

(2) We have also revised the relevant sentence to clarify the source of the bias. The Rayleigh equation itself is valid under its classical closed-system assumptions, where the reactant reservoir receives no external input and the product is removed by a fractionating reaction. The bias discussed here arises not from the Rayleigh equation itself, but from applying it directly over a finite CTM integration step in an open atmosphere. During a model time step, SO_2 is continuously affected by emissions, transport, deposition, dilution, mixing, and multi-pathway oxidation. Therefore, applying the Rayleigh equation over the full model time step can artificially amplify the isotope fractionation effect when the SO_2 conversion fraction within that step is large.

The iterative time-splitting method is therefore not intended to correct or modify the Rayleigh equation. Instead, it reduces numerical bias associated with time discretization and open-system mixing by dividing each SO_2 oxidation calculation into smaller conversion sub-steps and updating the isotopic composition iteratively. This keeps the conversion fraction within each sub-step small and makes the Rayleigh-based calculation a better numerical approximation of continuous isotope evolution in the open atmospheric system. We have revised the manuscript accordingly to avoid suggesting that the Rayleigh equation itself is the source of the bias.

The revised sentence in section 2.4.2 now reads: “To reduce the numerical bias that can arise when the Rayleigh equation is applied directly over a finite CTM time step in an open atmospheric system, we introduce an iterative time-splitting method that divides each oxidation calculation into smaller conversion sub-steps and updates the isotopic composition iteratively.”

Comment 8 (Page 16, Fig. 6)

Reviewer's Comment: Fig. 6 shows that the model doesn't always provide a reliable framework, e.g. discrepancies between simulation and observation in figure (c).

Author's Response: We thank the reviewer for this important comment. We agree that the discrepancies in Fig. 6(c) indicate limitations that should be discussed more explicitly. In the revised manuscript, we clarify that the validation of $\Delta\delta^{34}S\_SO_4^{2-}/SO_2$ and the validation of $\delta^{34}S\_SO_4^{2-}$ represent two different levels of model evaluation. $\Delta\delta^{34}S\_SO_4^{2-}/SO_2$ mainly reflects isotope fractionation during atmospheric oxidation and is therefore a more direct varial for evaluating the oxidation isotope module. In contrast, absolute $\delta^{34}S\_SO_4^{2-}$ is additionally affected by the isotopic composition of emitted SO_2, emission inventory uncertainties, meteorological transport, and mixing.

Therefore, the discrepancies in Fig. 6(c) do not necessarily indicate that the oxidation isotope module itself is unreliable. Rather, they reflect the combined influence of oxidation-module uncertainty and source-isotopic assumptions, especially the simplified assumption of $\delta^{34}S\_SO_2 = 0‰$ for anthropogenic emissions. To make this clearer, we have revised the Discussion section to separate oxidation-driven biases from source-driven biases and to discuss the limitations of the current framework more explicitly. We have also claimed that the model fully reproduces observed $\delta^{34}S\_SO_4^{2-}$, and now describe the model as capturing the general enrichment direction and broad variability while acknowledging site- and season-dependent discrepancies.

Comment 9 (Page 20)

Reviewer's Comment: The references Wei et al. (2024) and Wei et al. (2025) are not included in the references list.

Author's Response: Thank you. We have verified the complete information for these two references and added them to the reference list.

- Wei, L. (2024). The dataset of compiled observed and simulated sulfur isotopic composition (δ34S_SO2, δ34S_SO_4^{2-}) across Eastern China's cities. [Data set]. Zenodo. https://doi.org/10.5281/zenodo.14357423.
- Wei, L. (2025). Isotopic Chemistry Module Developed and Coupled with NAQPMS Model. Zenodo. https://doi.org/10.5281/zenodo.14724954.

Comment 10 (Supplement S1)

Reviewer's Comment: N and N* are not defined.

Author's Response: We have revised as: $N({}^{h}X)$ and $N({}^{l}X)$ represent the atomic abundances of the heavier stable isotope (${}^{h}X$) and lighter stable isotope (${}^{l}X$), respectively.

Comment 11 (Supplement S6)

Reviewer's Comment: This α is the same as in Eq. (3)? Rr is undefined.

Author's Response: Thank you for pointing out these inconsistencies.

(1) Yes, α is the same as in Eq. (3).

(2) We have added a definition for Rr. Rr is the stable isotope ratio of the reactant added to the reservoir during the interval.

Comment 12 (Supplement S9)

Reviewer's Comment: The derivation of the left-hand side is not clear.

Author's Response: We thank the reviewer for this comment. We have added intermediate steps to clarify the derivation of the left-hand side of Eq. S9.