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 1 (RC1)

Reviewer's Overall Comment:

This manuscript addresses an important limitation of conventional end-member mixing models in representing progressive isotopic evolution in complex atmospheric systems where mixing and reactions occur simultaneously. The development of an isotope-enabled chemical transport model and the iterative time-splitting strategy are potentially valuable methodological contributions. The discussion of isotopic fractionation during combustion and flue gas desulfurization (FGD) is also interesting and relevant to sulfur isotope source apportionment. However, the manuscript still has important weaknesses in internal consistency, model evaluation, manuscript organization, and figure presentation. In its current form, the paper does not yet clearly separate what is directly demonstrated by the isotope-enabled model from what is inferred from literature synthesis or conceptual interpretation. In addition, repeated problems in the figures, captions, and formatting suggest that the manuscript would benefit from a more careful and systematic revision before further consideration.

Author's Response: We thank the reviewer for this summary assessment. We fully acknowledge these concerns, which overlap with the specific points raised in the reviewer's detailed comments below. Corresponding revisions are described in our point-by-point responses to each individual comment below (see Major Comments 1–2 and Minor Comments 1–21). Briefly, these include: clearly distinguishing model-demonstrated results from literature-based inferences, revising the Abstract and Conclusions to more accurately reflect model skill, providing mechanistic explanations for site-specific biases, systematically improving all figures and captions, and correcting formatting and reference issues. We are committed to implementing all these revisions carefully.

Major Comment 1

Reviewer's Comment: The authors assign a uniform $\delta^{34}S$ value of 0‰ to all anthropogenic SO_2 emissions (Lines 178–179), while acknowledging that the actual isotopic composition of anthropogenic sources spans a range of −30‰ to +30‰ (Hoefs and Harmon, 2022). More importantly, one of the manuscript's central interpretive claims is that combustion processes cause a depletion of approximately −10‰ to −5‰ in emitted SO_2 relative to sulfur-containing fuels, yet this effect is not actually represented in the model framework. This creates an important internal inconsistency between model setup and interpretation. The authors should therefore distinguish much more clearly between conclusions supported directly by the isotope-enabled simulation and broader implications inferred from literature synthesis or conceptual discussion.

Author's Response: We thank the reviewer for identifying this important structural issue. We fully agree that the original manuscript did not distinguish clearly enough between model-demonstrated results and literature-based inferences. In the revised manuscript, we have restructured the relevant sections to make this boundary explicit.

(1) We have clarified the role of the $\delta^{34}S\_SO_2 = 0‰$ emission assumption in the revised manuscript. Setting $\delta^{34}S\_SO_2 = 0‰$ serves two purposes. First, because $\Delta\delta^{34}S\_SO_4^{2-}/SO_2$ is mathematically independent of the absolute emission $\delta^{34}S$, this assumption enables a direct source-independent evaluation of the oxidation module. Second, comparing simulated and observed $\delta^{34}S\_SO_4^{2-}$ under this assumption yields a deductive inference: the model reproduces observed sulfate $\delta^{34}S$ with $\delta^{34}S\_SO_2 \approx 0‰$, yet source fuel $\delta^{34}S$ across eastern China is documented at 1‰–10‰ (Hong et al., 1993; Guo et al., 2016; Chen et al., 2017). This discrepancy implies that emitted SO_2 is systematically ^{34}S-depleted relative to the source fuel, consistent with independent laboratory measurements of combustion and FGD isotopic fractionation ($\varepsilon^* \approx -5.5‰$; Derda et al., 2007).

(2) We agree with the reviewer that the combustion/FGD isotopic fractionation discussion (~−10‰ to −5‰ depletion in emitted SO_2 relative to fuels) is not directly simulated by the model — it is a literature-based synthesis drawing on independent experimental studies (Hong et al., 1993; Chen et al., 2017; Derda et al., 2007). The combustion/FGD fractionation is not a process that belongs inside an atmospheric CTM. In our model framework, gridded SO_2 emission fluxes are prescribed as input, and the $\delta^{34}S$ value of emitted SO_2 is an input parameter rather than a variable resolved inside the atmospheric chemistry solver. Consequently, combustion-induced fractionation should be incorporated during the preprocessing stage when constructing the isotope-tagged emission inventory. Based on our study, using coal $\delta^{34}S$ directly as a proxy for emitted $\delta^{34}S$ of SO_2, without correcting for combustion/FGD fractionation, would itself introduce a systematic input bias.

We have made the following revisions throughout the manuscript:

Methodology (Section 2.3). We added a description clarifying the $\delta^{34}S\_SO_2 = 0‰$ assumption: "We adopt a constant signature of $\delta^{34}S= 0‰$ V-CDT for SO_2 emission sources. This simplified assumption isolates the atmospheric chemical isotope effect from poorly constrained source signatures. Because the sulfur isotope difference between SO_2 and sulfate ($\Delta\delta^{34}S\_SO_4^{2-}/SO_2 = \delta^{34}S\_SO_4^{2-} - \delta^{34}S\_SO_2$), which approximates the apparent isotopic fractionation multiplied by 1000‰ and is hereafter referred to as the isotope effect, can be applied to validate the oxidation module of isotope-enabled CTM. By contrast, the $\delta^{34}S\_SO_2$ and $\delta^{34}S\_SO_4^{2-}$ values depend on the prescribed emission signature; direct comparisons between simulated and observed $\delta^{34}S\_SO_2$ and $\delta^{34}S\_SO_4^{2-}$ are therefore subject to the uncertainties of this simplified assumption and should be interpreted with caution. Jointly examining the simulated and observed $\delta^{34}S\_SO_2$ and $\delta^{34}S\_SO_4^{2-}$ together with $\Delta\delta^{34}S\_SO_4^{2-}/SO_2$ provides a diagnostic of whether a given model–observation bias arises primarily from the atmospheric oxidation processes or from the assumed emission-source signatures. "

Discussion structure (Section 4). The Discussion is now split into two sections with explicit boundaries. Section 4.1 is titled "Model-demonstrated results: oxidation-driven versus source-driven biases" and focuses exclusively on what the model directly simulates: the overestimation of $\Delta\delta^{34}S\_SO_4^{2-}/SO_2$ attributed to underrepresented TMI-catalyzed oxidation, and the two-category classification of $\delta^{34}S\_SO_4^{2-}$ biases (Category 1 — oxidation-driven; Category 2 — source-driven at Beijing winter). Section 4.2 is titled "Interpretive implications: combining model results with literature evidence" and opens with a clear transition paragraph:

"The preceding discussion reflects what is directly resolved by the isotope-enabled model. We now extend the discussion to broader implications inferred by combining our model results with literature evidence on emission-source isotopic signatures, combustion fractionation, and FGD. "

Conclusions (Section 5). The deductive chain is now explicit and avoids implying that combustion/FGD fractionation was simulated. The key revised passage states:

"Taken together with the documented higher $\delta^{34}S$ values of coal (1‰–10‰), the model's ability to reproduce observed $\delta^{34}S\_SO_4^{2-}$ under the $\delta^{34}S\_SO_2 = 0‰$ emission assumption implies that combustion- and FGD-related ^{34}S depletion in emitted SO_2 ($\varepsilon^* \approx -5.5‰$; Derda et al., 2007) is largely counterbalanced by the ^{34}S enrichment during atmospheric SO_2 oxidation ($\Delta\delta^{34}S \approx +6$ to $+8‰$). This counterbalancing explains why ambient sulfate $\delta^{34}S$ is often close to that of sulfur-containing fuels. Neglecting the emission-side fractionation therefore introduces systematic bias into isotope-based source apportionment, underestimating the contribution of fuels with significant combustion fractionation while overestimating sources with $\delta^{34}S$ near 0‰. Our study highlights that incorporating both emission-side and oxidation-side fractionation into source apportionment frameworks is therefore essential for reliable results."

Major Comment 2

Reviewer's Comment: The model shows substantial site- and season-dependent bias in $\Delta\delta^{34}S\_SO_4^{2-}/SO_2$, including strong overestimation in Nanjing winter and Tianjin summer, but also underestimation in other cases such as Beijing winter. Under these circumstances, the Abstract statement that the model can "reproduce the sulfur isotope effect" is too strong. The authors should revise the Abstract and Conclusions to reflect the actual level of model skill more accurately, and they should discuss the likely causes of these mismatches in more mechanistic detail rather than attributing them mainly to emission inventory uncertainty.

Author's Response: We thank the reviewer for this careful and constructive assessment. We fully agree that the Abstract and Conclusions should more accurately reflect the model's skill, and that site- and season-dependent biases require mechanistic detail. The specific revisions are as follows.

(1) Abstract and Conclusions have been revised to report both observed and simulated values and to acknowledge the systematic overestimation (see Minor Comment 14 for the revised text).

(2) Mechanistic interpretation. We evaluate the model through a two-step framework that separates oxidation-pathway performance from emission-source effects:

Step 1 — Validating the oxidation module via $\Delta\delta^{34}S\_SO_4^{2-}/SO_2$ at Nanjing.

Because $\Delta\delta^{34}S$ is independent of emission $\delta^{34}S$, it provides an oxidation-module test. At Nanjing, the model captures the enrichment direction and seasonal variation but systematically overestimates the magnitude (NMB = 35–55%). This overestimation is attributed to the underrepresented TMI-catalyzed oxidation pathway ($\alpha = 0.9949$, $\varepsilon \approx -5.1‰$) — the only channel that produces ^{34}S-depleted sulfate. Its contribution is underestimated in current CTMs (Alexander et al., 2009; Itahashi et al., 2022; Shao et al., 2019), and our model does not yet include TMI-catalyzed oxidation in aerosol liquid water, which likely contributes to the remaining bias. This diagnosis is discussed in Sections 3.2.1 and 4.

Step 2 — Evaluating $\delta^{34}S\_SO_4^{2-}$ across multiple sites reveals two distinct bias categories:

Category 1 — Oxidation-driven biases (Nanjing, Hangzhou, Tianjin): $\delta^{34}S\_SO_4^{2-}$ biases are broadly consistent in direction with the known $\Delta\delta^{34}S$ overestimation, confirming that the $\delta^{34}S\_SO_2$ = 0‰ assumption is reasonable for well-mixed regional emissions at these sites, with remaining residuals driven by underrepresented TMI and multiphase pathways.

Category 2 — Source-driven bias (Beijing winter): the model underestimates $\delta^{34}S\_SO_4^{2-}$ by ~50% (NMB = −50.5%) despite the oxidation module's upward $\Delta\delta^{34}S$ bias. This reversal cannot be explained by oxidation-module error and instead indicates failure of the $\delta^{34}S\_SO_2$= 0‰ assumption, consistent with the elevated coal $\delta^{34}S$ in the Beijing–Hebei–Henan region (3.5‰–16.1‰) and enhanced wintertime residential coal combustion (~46% of monthly $PM_{2.5}$; Zhang et al., 2017). Additional details, including quantitative discussion and mechanistic attribution, are provided in the revised Section 4.1.

We believe these revisions provide the mechanistic detail requested while accurately conveying both the model's ability and its limitations.

Minor Comment 1 (Lines 30–31, 547)

Reviewer's Comment: The manuscript states that the model reproduces "the observed mean sulfur isotope effect ($\Delta\delta^{34}S\_SO_4^{2-}/SO_2$ = 3.43 ± 1.11‰)". However, 3.43‰ is the observed mean value, not the simulated one. The current phrasing is misleading.

Author's Response: We thank the reviewer for pointing out this phrasing issue. We agree that the previous wording was misleading. The value of 3.43 ± 1.11‰ refers to the observed mean $\Delta\delta^{34}S\_SO_4^{2-}/SO_2$, not the simulated value. In the revised manuscript, we have corrected the relevant sentences throughout the Abstract, Results, and Conclusions to clearly distinguish between observed and simulated sulfur isotope effects.

The revised Abstract now reads: "Validation against compiled observation data demonstrates the model successfully reproduces the sulfur isotope enrichment of sulfate relative to SO_2 and captures the spatial patterns and seasonal variability of the sulfur isotope effect across eastern China (simulated $\Delta\delta^{34}S\_SO_4^{2-}/SO_2$ = 6.11±1.85‰; observed = 3.43±1.11‰)."

In Section 3.2.1, we revised the relevant text as follows: "The overall simulated $\Delta\delta^{34}S\_SO_4^{2-}/SO_2$ is 6.11 ± 1.85‰, compared to the observed mean of 3.43 ± 1.11‰. The model thus captures the enrichment direction and seasonal variation of the sulfur isotope effect but systematically overestimates its magnitude."

The revised Conclusions now reads: "The model captures the ^{34}S enrichment in sulfate and the spatial and seasonal patterns of the sulfur isotope effect across eastern China (simulated $\Delta\delta^{34}S\_SO_4^{2-}/SO_2$ = 6.11±1.85‰; observed = 3.43±1.11‰)."

These revisions ensure that the observed and simulated values are clearly distinguished and that the model performance is described more accurately.

Minor Comment 2 (Lines 64–66)

Reviewer's Comment: The authors identify reliance on the Rayleigh distillation equation as one reason for discrepancies in prior studies. However, the present model also relies on a Rayleigh-type framework, albeit with iterative time-splitting. The authors should discuss this limitation more explicitly.

Author's Response: We agree with the reviewer and have revised the manuscript to explicitly discuss this limitation. This discussion is now presented in Section 2.4.2 as follows:

"The classical Rayleigh distillation equation assumes that (i) the product, once formed, is immediately and irreversibly removed from the reactant reservoir with no further isotopic exchange, and (ii) the reservoir receives no external input, with reactants consumed solely by the fractionating reaction. These assumptions are invalid in the open atmosphere, where the reactant reservoir within each grid cell is continuously influenced by emissions, advection, and diffusive mixing during a single integration step (~30 min). Because mixing and fractionation occur simultaneously, applying the Rayleigh equation over the full-time step—especially under a large conversion fraction—makes the isotopic composition of the product and residual reactant depend sensitively on the residual fraction f_{rem}, which is itself influenced by time discretization and reaction-rate constants. This artificially amplifies the apparent enrichment/depletion in the residual reactant—the so-called reservoir effect—and provides the numerical motivation for the iterative time-splitting method used in this study."

We further illustrate this with Figure 3 and Figure S1, showing that the reservoir effect produces unrealistically large apparent isotope fractionations as the reactant approaches depletion, and that the combined effects of mixing and fractionation in an open system reduce the $\Delta\delta^{34}S$ variation relative to the classical Rayleigh prediction. To mitigate this bias, we introduce an iterative time-splitting method that decomposes each integration step into smaller sub-steps with intermediate re-mixing.

We also acknowledge the reviewer's important point that our iterative time-splitting method still relies on a Rayleigh-type framework. Within each sub-step, we still assume a closed system (no external input) and use the Rayleigh equation to compute isotopic fractionation. We compare the iterative method against an exact integration solution for an open system (Text S3). Through sensitivity analysis, we find that when the sub-step size is sufficiently small (limiting the reaction fraction to ~2% per sub-step), the discrepancy between the Rayleigh-based splitting method and the exact open-system solution is less than 0.3‰, which is comparable to the average analytical precision of isotope measurements. This confirms that the chosen sub-step size is acceptable for reducing simulation bias, and we have adopted this value to improve the simulation.

These points are presented in Section 2.4.2 and Section 3.1 of the revised manuscript, where we state clearly that our method remains Rayleigh-based and that the iterative splitting only mitigates, rather than fully resolves, the reservoir effect. We thank the reviewer for pushing us to clarify this point.

Minor Comment 3 (Lines 121–122)

Reviewer's Comment: Tense inconsistency. "The simulation began in March 2014. The initial 3 months serve as a spin-up time." Should read "served".

Author's Response: Thank you. We have changed "serve" to "served" for tense consistency.

Minor Comment 4 (Line 172)

Reviewer's Comment: The URL for the MEIC emission inventory is incorrectly formatted as "http:// http://meicmodel.org.cn/..." with the protocol prefix duplicated.

Author's Response: We have corrected the duplicated "http://" prefix in the URL.

Minor Comment 5 (Lines 309–310)

Reviewer's Comment: If the overall net sulfur isotope fractionation factor $\alpha^{34}S\_S(IV)$ = 1.0063 at 0°C is parameterized using pathway contributions derived from GEOS-Chem rather than diagnosed directly from NAQPMS, this should be stated explicitly.

Author's Response: Thank you for this constructive suggestion. In the revised manuscript, we have explicitly stated that the overall fractionation factor $\alpha^{34}S\_S(IV)$ = 1.0063 at 0 °C is derived from the GEOS-Chem model results of Shao et al. (2019), not directly diagnosed from NAQPMS.

Revised as follows: "To illustrate the magnitude of the reservoir effect under realistic atmospheric conditions, we consider the competing S(IV) oxidation pathways: gas-phase OH radicals, aqueous-phase H_2O_2, O_3, and TMI-catalysis, and heterogeneous reaction. Using model results from Shao et al. (2019), who employed the GEOS-Chem model to quantify the contributions of these competing pathways to sulfate formation during a Beijing pollution episode. The reported contributions are 42.6%, 2.2%, 1.3%, 27.2%, and 26.7%, respectively."

We also acknowledge that the current NAQPMS does not explicitly output sulfate production from individual oxidation pathways; this will be addressed in future work by implementing a pathway-tracking scheme.

Minor Comment 6 (Lines 383–384)

Reviewer's Comment: Subject–verb agreement error. "Figure 4 and 5 shows..." should read "Figures 4 and 5 show..."

Author's Response: Thank you. We have changed "shows" to "show".

Minor Comment 7 (Lines 508–511)

Reviewer's Comment: The discussion linking the post-1999 decline in $\delta^{34}S\_SO_4^{2-}$ at Tsuruoka, Japan to FGD technology adoption is suggestive, but temporal correlation alone does not establish causation.

Author's Response: We agree with the reviewer that temporal correlation does not establish causation. We have revised the relevant paragraph as follows:

(a) "This likely contributes to" has been replaced with "are temporally consistent with" to avoid implying a causal relationship;

(b) We have added a note acknowledging that other concurrent factors — such as changes in source composition, shifts in the geographic distribution of SO_2 emissions, and variations in atmospheric oxidation pathways — may also have contributed to the observed $\delta^{34}S$ decline;

(c) We have explicitly stated that establishing a direct causal linkage between FGD deployment and the $\delta^{34}S$ decline would require a dedicated study combining long-term field observations with systematic source sampling and experimental study of isotopic fractionation during combustion and FGD processes. We nevertheless note that the temporal coherence between FGD adoption and the $\delta^{34}S$ decline is suggestive and worth further investigation.

Minor Comment 8 (Throughout)

Reviewer's Comment: Notation for $\delta^{34}S\_SO_4^{2-}$ is inconsistent ($\delta^{34}SO_4^{2-}$ vs. $\delta^{34}S\_SO_4^{2-}$). Similarly, "$\Delta\delta^{34}S$" and "$\delta^{34}S$" are used interchangeably.

Author's Response: Thank you for pointing this out. We have unified the notation throughout the manuscript to use $\delta^{34}S\_SO_4^{2-}$, $\delta^{34}S\_SO_2$, and $\Delta\delta^{34}S\_SO_4^{2-}/SO_2$ as the standard symbols.

Minor Comment 9 (Throughout)

Reviewer's Comment: Equation reference formats are inconsistent ("Equation (4)" vs. "eq. 9–10").

Author's Response: Thank you. We have unified the format to "Equation (N)" throughout the manuscript.

Minor Comment 10 (Throughout)

Reviewer's Comment: Capitalization of "Eastern China" is inconsistent.

Author's Response: We have standardized to "eastern China" throughout.

Minor Comment 11 (Reference list)

Reviewer's Comment: Wei et al. (2018a) and (2018b) appear to refer to the same published article. This duplication should be corrected.

Author's Response: Thank you. We have merged these two entries in the reference list as Wei et al. (2018) and verify the completeness of the author list, as follows: Wei, L., Yue, S., Zhao, W., Yang, W., Zhang, Y., Ren, L., Han, X., Guo, Q., Sun, Y., Wang, Z., and Fu, P.: Stable sulfur isotope ratios and chemical compositions of fine aerosols (PM2.5) in Beijing, China, Sci. Total Environ., 633, 1156-1164, https://doi.org/10.1016/j.scitotenv.2018.03.153, 2018.

Minor Comment 12

Reviewer's Comment: The manuscript interweaves three layers: method development, model evaluation, and interpretive implications. These should be more clearly separated.

Author's Response: We agree with the reviewer's suggestion that the three layers—method development, model evaluation, and interpretive implications—should be more clearly separated. We have made the following revisions to the manuscript:

(1) A transitional paragraph has been added at the beginning of Section 3 (Results), framing the evaluation as a two-stage process: validation of the numerical method followed by comparison with observations.

(2) Interpretive discussions previously embedded in Sections 3.2.1 and 3.2.2 (e.g., explanations for the overestimation of $\Delta\delta^{34}S$ and the Beijing winter underestimation) have been relocated to Section 4 (Discussion), ensuring that the Results section focuses strictly on model evaluation.

(3) A transitional paragraph has been added at the beginning of Section 4, bridging from model evaluation to interpretive implications.

Minor Comment 13

Reviewer's Comment: The Results section sometimes moves too quickly from describing model behavior to broader mechanistic interpretation.

Author's Response: We thank the reviewer for this helpful comment. We agree that some parts of the original Results section moved too quickly from describing model behavior to broader mechanistic interpretation. In the revised manuscript, we have carefully separated direct model-demonstrated results from broader interpretive discussion.

Specifically, the Results section has been revised to focus on model performance, simulated $\delta^{34}S\_SO_4^{2-}$ patterns, oxidation-pathway contributions, and the comparison between simulated and observed $\Delta\delta^{34}S\_SO_4^{2-}/SO_2$. Broader interpretations concerning the causes of site- and season-dependent $\delta^{34}S\_SO_4^{2-}$ biases, the influence of source-isotopic assumptions, and the implications of combustion/FGD-related isotope fractionation have been moved to the Discussion section.

This revision is consistent with the broader structural changes described in our responses to Major Comments 1 and 2. In response to Major Comment 1, we clarified the model design with assumption of $\delta^{34}S\_SO_2$ emissions = 0‰, and distinguish much more clearly between conclusions supported directly by the isotope-enabled simulation and broader implications inferred from literature synthesis or conceptual discussion. In response to Major Comment 2, we reorganized the discussion of site- and season-dependent $\delta^{34}S\_SO_4^{2-}$ biases into two categories: oxidation-driven biases and source-driven biases. This revised structure helps distinguish model-demonstrated oxidation effects from broader source-related interpretations.

Accordingly, the revised Results section now presents the model outputs more descriptively, while the mechanistic implications are discussed in the Discussion section with appropriate support from the model results, observational comparisons, and literature evidence. This change improves the logical flow of the manuscript and avoids overinterpreting the results before the relevant uncertainties and assumptions are fully discussed.

Minor Comment 14

Reviewer's Comment: The title, abstract, and conclusions appear stronger than the actual level of evidence. The phrase "revealing the overlooked isotopic fractionation" reads as though directly resolved by the model.

Author's Response: We agree with the reviewer. We acknowledge that the original title, abstract, and conclusions overstated the level of evidence. Particularly, the combustion/FGD isotopic fractionation is not directly simulated by our model. Rather, it is demonstrated through a deductive chain: the model reproduces observed $\delta^{34}S\_SO_4^{2-}$ under the $\delta^{34}S\_SO_2 = 0‰$ emission assumption, yet coal $\delta^{34}S$ is known to be 1‰–10‰ across eastern China — implying that emitted SO_2 is systematically depleted in ^{34}S, consistent with literature-documented combustion/FGD fractionation. We have revised the manuscript to reflect this model–literature deductive chain rather than implying direct model result. The specific revisions are as follows:

(1) The subtitle "Revealing the Overlooked Isotopic Fractionation During Combustion and Gas Desulfurization" has been revised to "Demonstrating the Overlooked Isotopic Fractionation During Combustion and Flue Gas Desulfurization." We replaced "Revealing" with "Demonstrating" because the combustion/FGD fractionation is not a direct model output.

(2) Abstract: The original sentence "Further, our study underscores the importance of considering isotopic fractionation during combustion and chemical processes for accurate source apportionment" has been revised as: "Further, the agreement between simulated (with $\delta^{34}S\_SO_2 = 0‰$ emission assumption) and observed sulfate isotopic compositions, combined with the documented higher $\delta^{34}S$ values of coal at 1‰–10‰ across eastern China, implies a systematic ^{34}S depletion in emitted SO_2 relative to fuels. This highlights the importance of considering isotopic fractionation during combustion, flue gas desulfurization and chemical processes for accurate source apportionment." The abstract now makes clear that the combustion/FGD isotopic fractionation is logically derived from the model–literature comparison, not from direct model output.

(3) Conclusions: The original sentences "Combined with literature data, our results further indicate that combustion and flue gas desulfurization deplete SO_2 in ^{34}S (–10‰ to –5‰) relative to fuels ($\delta^{34}S$ = 1‰–10‰), corresponding to a net fractionation of $\varepsilon^* \approx -5.5‰$. " have been revised as: " Taken together with the documented higher $\delta^{34}S$ values of coal (1‰–10‰), the model's ability to reproduce observed $\delta^{34}S\_SO_4^{2-}$ under the $\delta^{34}S\_SO_2 = 0‰$ emission assumption implies that combustion- and FGD-related ^{34}S depletion in emitted SO_2 ($\varepsilon^* \approx -5.5‰$; Derda et al., 2007) is largely counterbalanced by the ^{34}S enrichment during atmospheric SO_2 oxidation ($\Delta\delta^{34}S \approx +6$ to $+8‰$). This counterbalancing explains why ambient sulfate $\delta^{34}S$ is often close to that of sulfur-containing fuels."

Throughout these revisions, we have clearly distinguished between results directly derived from model simulations and conclusions that are logically deduced from the model–literature comparison.

Minor Comment 15

Reviewer's Comment: The Supporting Information requires substantial formatting correction. Several equations in the derivation section are not properly rendered.

Author's Response: We have carefully reviewed and revised the Supporting Information to correct the formatting issues. Specifically, we have ensured that all equations in the derivation section are properly rendered and that variable notation is consistent with the main text.

Minor Comment 16

Reviewer's Comment: Some important method-validation content is currently relegated to the Supporting Information. The main text should more clearly summarize why the iterative time-splitting method is needed and how much bias it reduces.

Author's Response: We thank the reviewer for this helpful suggestion. We agree that the rationale and validation of the iterative time-splitting method should be more clearly summarized in the main text. In the revised manuscript, we have clarified in Section 2.4.2 that the Rayleigh-equation bias arises when isotope fractionation is calculated over a large SO_2 conversion fraction in an open atmospheric system, where SO_2 is continuously affected by emissions, transport, deposition, dilution, and multi-pathway oxidation. This motivates the iterative time-splitting method, which divides each SO_2 oxidation calculation into smaller conversion sub-steps and updates the isotopic composition iteratively.

We have also added a concise summary of the numerical comparison between the direct Rayleigh calculation and the iterative method. "The largest differences occur mainly over remote regions, such as oceanic areas, where SO_2 emissions are low, reaction extents are great, and the SO_2 reservoir effect is strongest. In these regions, the iterative method reduces the simulated $\Delta\delta^{34}S\_SO_4^{2-}/SO_2$ by approximately 1.5‰–3.0‰ relative to the direct Rayleigh calculation applied over the full model time step. In regions with intensive anthropogenic activity, the effect is smaller but still non-negligible; in some polluted areas, the optimized algorithm changes the simulated $\Delta\delta^{34}S\_SO_4^{2-}/SO_2$ by approximately 0.3‰–1.0‰. These revisions clarify why the iterative time-splitting method is needed and quantify the magnitude of the bias reduction."

These revisions make clear why the iterative time-splitting method is needed and quantify the magnitude of the bias reduction. The detailed validation results remain in the Supporting Information.

Minor Comment 17 (Figure 1)

Reviewer's Comment: Figure 1 contains several problems: unexplained symbol near Mongolia, legend-text inconsistency ("wet precipitation" vs. "precipitation"), domain inconsistency with subsequent figures.

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

(1) The symbol near Mongolia represents the literature-reported $\delta^{34}S$ value of coal samples from Inner Mongolia, not aerosol sulfate or precipitation sulfate observations. This region lacks available $\delta^{34}S$ observations for aerosol sulfate and precipitation sulfate in our compiled dataset; therefore, only the coal $\delta^{34}S$ data are shown. Because the regional mean coal $\delta^{34}S$ value is close to 0‰ (~0.8‰), the corresponding bar appears small and was not visually prominent in the original figure.

(2) We have unified "precipitation" terminology to "wet precipitation" between the legend and caption;

(3) We have checked the spatial domains for consistency: Figure 1, Figures 4 and 5 display results over domain D1, while Figure 6(a) shows results over domain D2.

Minor Comment 18 (Figures 3–5)

Reviewer's Comment: Figures 3–5 are not clearly labeled, captions do not match figure structure, sub-panel labels are insufficiently clear.

Author's Response: We thank the reviewer for this comment. We have revised Figures 3–5 to ensure sub-panel labels are clearly visible and captions fully describe the figure structure. For Figure 3, we added the panel labels and clarified the line types. For Figures 4 and 5, we added the panel labels and revised the captions to state the sensitivity experiment design and the meaning of positive and negative $\delta^{34}S$ values for each panel. The Figure 5 caption was also rewritten as a self-contained description rather than a brief cross-reference to Figure 4.

Minor Comment 19 (Figure 6)

Reviewer's Comment: Figure 6 is difficult to interpret because of unexplained boundary elements and insufficient visual differentiation between summer/winter and simulated/observed data.

Author's Response: We thank the reviewer for this comment. We have revised Figure 6 to address these issues.

We have improved the contrast between summer and winter and between simulated and observed data. In panel (a), summer and winter are displayed in separate rows with clearly labeled seasonal headers. In panels (b) and (c), simulated and observed data are distinguished by different marker symbols and colors, and a legend explicitly identifies each data type.

Minor Comment 20

Reviewer's Comment: Several figure captions are too compressed and depend too heavily on the main text. Each figure should be largely self-explanatory.

Author's Response: We thank the reviewer for this suggestion. In the revised manuscript, we have expanded all figure captions to include variable definitions, data sources, panel descriptions, color/symbol meanings. These revisions are detailed in the relevant section of the revised manuscript and are also reflected in our responses to Minor Comments 17–19 and Comments 4, 8, and the associated figure-specific comments. The revised captions now allow each figure to be understood largely independently, without requiring the reader to refer back to the main text for basic information.

Minor Comment 21

Reviewer's Comment: Across the main figures, the visual language should be standardized: color-bar direction, enrichment/depletion color logic, seasonal labels, and simulated-vs-observed symbols.

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

In the revised manuscript, we have standardized the visual language across all main figures. The color-bar direction is now consistent, with warm colors representing ^{34}S enrichment and cool colors representing depletion. Seasonal labels follow a uniform format (summer: June–August; winter: December–February). In model–observation comparison panels, simulated and observed data are distinguished by a consistent set of marker symbols and colors, with a legend explicitly identifying each data type. These changes ensure a coherent visual experience across all figures.