Response to Reviewer's comments

All responses and revisions in the revised manuscript are identified in **blue** text color.

Reviewer#1's comments:

1. Lines 31-32: What do the letters "a, b, c, d" in the text "$\delta^{34}S$=a, $\delta^{34}S$=b, $\delta^{34}S$=c, $\delta^{34}S$=d" represent?

Response: While regretting this initial confusion, the letters "a," "b," "c," and "d" have been entirely omitted from the revised manuscript, as these characters served no scientific purpose and were legacy remnants from an earlier draft. For more clarity, we have added/revised these sentences as following.

Page 2, Lines 45-48 in the revised manuscript:

Contemporary research has quantitatively established the sulfur isotopic signatures ($\delta^{34}S$) associated with major atmospheric oxidation routes, including transition metalion-catalyzed (TMI), ozone-mediated (O_3), nitrogen oxide-driven (NO_x), and hydrogen peroxide-initiated (H_2O_2) pathways, through systematic analysis of particulate matter samples.

2. Lines 35-38: Please clarify the distinction between complete and incomplete SO_2 oxidation frameworks.

Response: We sincerely appreciate the reviewers' valuable comments, which allow us to clarify the theoretical underpinnings of our methodology. To interpret the isotopic dynamics effectively, we established two contrasting frameworks. The Complete Oxidation (CO) Process acts as an idealized baseline, operating on the premise that all gaseous SO_2 is exhaustively converted to particulate sulfate, yielding a sulfur oxidation ratio (SOR) of 1. Consequently, this framework directly equates the calculated source isotopic signature ($\delta^{34}S$-source) to the measured sulfate value ($\delta^{34}S$-SO_4^{2-}), intentionally omitting the isotopic fractionation kinetics that govern the oxidation pathway. In contrast, the Incomplete Oxidation (InCO) Process reflects actual atmospheric conditions, specifically the reality that SO_2-to-sulfate conversion is inherently partial (SOR<1). Grounded in the Rayleigh fractionation model, this framework synchronously integrates the observed isotopic values of gaseous SO_2 and

particulate SO_4^{2-} with the corresponding SOR. By doing so, it inversely derives more realistic source isotopic signatures alongside the kinetic fractionation factors (α), a conceptual advancement that forms the core innovation of our study. For more clarity, we have added/revised these sentences as following.

Page 6, Lines 159-166 in the revised manuscript:

The Complete Oxidation (CO) Process acts as an idealized baseline, operating on the premise that all gaseous SO_2 is exhaustively converted to particulate sulfate, yielding a sulfur oxidation ratio (SOR) of 1. Consequently, this framework directly equates the calculated source isotopic signature (δ^{34}S-source) to the measured sulfate value ($\delta^{34}S\text{-}SO_4^{2-}$), intentionally omitting the isotopic fractionation kinetics that govern the oxidation pathway. In contrast, the Incomplete Oxidation (InCO) Process reflects actual atmospheric conditions, specifically the reality that SO_2-to-sulfate conversion is inherently partial (SOR<1). Grounded in the Rayleigh fractionation model, this framework synchronously integrates the observed isotopic values of gaseous SO_2 and particulate SO_4^{2-} with the corresponding SOR. By doing so, it inversely derives more realistic source isotopic signatures alongside the kinetic fractionation factors (α), a conceptual advancement that forms the core innovation of our study.

3. Lines 65-69: The uncertainties for water-soluble ions, δ^{34}S and δ^{18}O are necessary to show in this part. In addition, please add the standard materials for measurements.

Response: We sincerely appreciate the reviewer for this insightful comment regarding our analytical protocols for water-soluble ions and stable isotopes (δ^{34}S and δ^{18}O). To ensure robust data quality, the analytical precision for all major water-soluble ions was rigorously verified via replicate measurements, consistently yielding values better than 5%. For the isotopic composition, results are reported in standard delta notation relative to international reference scales, specifically, Vienna Canyon Diablo Troilite (V-CDT) for δ^{34}S and Vienna Standard Mean Ocean Water (V-SMOW) for δ^{18}O, as formulated in Eq. (1) and (2). Notably, our analytical system demonstrated high stability, with long-term reproducibility constrained to better than 0.2‰ and 0.3‰ for sulfur and oxygen isotopes, respectively[1-2].

$$\delta^{34}S(‰) = \left[\left(^{34}S/^{32}S\right)_{sample}/\left(^{34}S/^{32}S\right)_{reference} - 1\right] \times 1000 \quad (1)$$

$$\delta^{18}O(‰) = \left[\left(^{18}O/^{16}O\right)_{sample}/\left(^{18}O/^{16}O\right)_{reference} - 1\right] \times 1000 \quad (2)$$

For more clarity, we have added/revised these sentences as following.

Page 3-4, Lines 97-104 in the revised manuscript:

To ensure robust data quality, the analytical precision for all major water-soluble ions was rigorously verified via replicate measurements, consistently yielding values better than 5%. For the isotopic composition, results are reported in standard delta notation relative to international reference scales, specifically, Vienna Canyon Diablo Troilite (V-CDT) for $\delta^{34}S$ and Vienna Standard Mean Ocean Water (V-SMOW) for $\delta^{18}O$, as formulated in Eq. (1) and (2). Notably, our analytical system demonstrated high stability, with long-term reproducibility constrained to better than 0.2‰ and 0.3‰ for sulfur and oxygen isotopes, respectively.

$$\delta^{34}S(‰) = \left[\left(^{34}S/^{32}S\right)_{sample}/\left(^{34}S/^{32}S\right)_{reference} - 1\right] \times 1000 \quad (1)$$

$$\delta^{18}O(‰) = \left[\left(^{18}O/^{16}O\right)_{sample}/\left(^{18}O/^{16}O\right)_{reference} - 1\right] \times 1000 \quad (2)$$

4. Lines 66-67: The sentence "The $\delta^{34}S$ value of sulfate was determined by precipitating $BaSO_4$ via $BaCl_2$ addition, followed by selective dissolution of residual $BaSO_3$ with 1 MHCl" is vague. Please rewrite it.

Response: Acknowledging this oversight, we are deeply grateful to the reviewers for their meticulous assessment, which directly prompted a comprehensive rewriting of the corresponding descriptions to ensure absolute clarity in the revised manuscript.

For the determination of sulfate $\delta^{34}S$ values, water-soluble sulfate within the filter extracts was initially isolated as $BaSO_4$ through the addition of an excess $BaCl_2$ solution. Because the sampling matrix inevitably captures both sulfate and sulfite, the latter originating from ambient SO_2, a targeted purification protocol was introduced; specifically, treating the co-precipitate with 1 M HCl selectively dissolved any residual $BaSO_3$ while leaving the acid-insoluble $BaSO_4$ intact. Following collection via filtration, the purified precipitate was rinsed thoroughly with deionized water until completely free of chloride ions and subsequently dried. To eliminate potential organic

interferences prior to isotopic interrogation, the dried $BaSO_4$ underwent thermal treatment in a muffle furnace at 1073 K for 2 hours.

For more clarity, we have added/revised these sentences as following.

Page 3, Lines 83-90 in the revised manuscript:

For the determination of sulfate $\delta^{34}S$ values, water-soluble sulfate within the filter extracts was initially isolated as $BaSO_4$ through the addition of an excess $BaCl_2$ solution. Because the sampling matrix inevitably captures both sulfate and sulfite, the latter originating from ambient SO_2, a targeted purification protocol was introduced; specifically, treating the co-precipitate with 1 M HCl selectively dissolved any residual $BaSO_3$ while leaving the acid-insoluble $BaSO_4$ intact. Following collection via filtration, the purified precipitate was rinsed thoroughly with deionized water until completely free of chloride ions and subsequently dried. To eliminate potential organic interferences prior to isotopic interrogation, the dried $BaSO_4$ underwent thermal treatment in a muffle furnace at 1073 K for 2 hours.

5. Lines 194-201: Wang et al. (2016) suggest that the aqueous oxidation of SO_2 by NO_2 is key to efficient sulfate formation, but is only feasible under two atmospheric conditions: on fine aerosols with high relative humidity and NH_3 neutralization or under cloud conditions. How to prove that the NO_2-mediated oxidation pathway is ubiquitous during the sampling period?

Response: We sincerely appreciate the reviewer for highlighting this critical point and directing our attention to the seminal work by Wang et al. (2020) and Wang et al (2016). We completely agree with the growing scientific consensus that the aqueous oxidation of SO_2 mediated by NO_2 is highly sensitive to aerosol liquid water content and pH, making it particularly potent during winter fog and haze conditions. Upon carefully reevaluating our data presentation in Figure 4, we realize that displaying solely the relative percentage contributions inadvertently masked the actual seasonal dynamics of this chemical pathway. While the fractional proportion of the NO_2^- mediated pathway appears visually comparable between winter and summer in our isotopic distribution, the absolute mass of sulfate generated via this route differs drastically. Our field measurements demonstrate that total particulate sulfate

concentrations peak at 27.55 ± 14.36 μg/m^3 during severe haze events, which predominantly occur in winter. Consequently, when translating these relative fractions into absolute mass concentrations, the NO_2 pathway produces a substantially higher burden of particulate sulfate in winter compared to summer. This mass-based dynamic aligns perfectly with the enhanced wintertime activity reported by Wang et al. (2020) and Wang et al (2016) and the broader field-based consensus. Furthermore, the sustained relative fraction of the NO_2 pathway during the summer months in Nanjing is not an artifact of our isotopic model, but rather a direct reflection of the region's specific emission inventory. As indicated by our $[NO_3^-]/[SO_4^{2-}]$ mass ratio analysis, which yielded values spanning from 0.15 to 1.95, with a mean of 0.98 ± 0.42, mobile vehicular emissions constitute a major atmospheric driver in this region. When these continuous, high-volume NO_x emissions couple with the incomplete SO_2 oxidation regimes characteristic of our summer study site, the NO_2 pathway maintains a significant fractional foothold, even though the absolute sulfate yield remains much lower than in winter. To eliminate this apparent contradiction and integrate the reviewer's excellent insights, we have thoroughly revised the discussion section corresponding to Figure 4 to explicitly distinguish between relative pathway fractions and absolute sulfate mass yields. We formally incorporated Wang et al. (2020) and Wang et al (2016) into the text, detailing how our absolute concentration metrics strongly corroborate their lab- and field-based findings regarding enhanced wintertime NO_2 oxidation. We expanded the narrative to clarify how local vehicular NO_x emissions sustain the relative percentage of this pathway during summer, ensuring the isotopic model results are properly contextualized within the region's specific atmospheric chemistry.

Reference:

[1] Wang, G., Zhang, R., Gomez, M. E., Yang, L., Levy Zamora, M., Hu, M., Lin, Y., Peng, J., Guo, S., Meng, J., Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Li, G., Wang, J., Tian, P., Marrero-Ortiz, W., Secrest, J., Du, Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Ji, Y., Zhang, F., Rosenfeld, D., Liss,

P. S., Duce, R. A., Kolb, C. E., and Molina, M. J.: Persistent sulfate formation from London Fog to Chinese haze, P. Natl. Acad. Sci. USA, 113, 13630–13635, https://doi.org/10.1073/pnas.1616540113, 2016.

[2] Wang, J., Li, J., Ye, J., Zhao, J., Wu, Y., Hu, J., Liu, D., Nie, D., Shen, F., Huang, X., Huang, D., Ji, D., Sun, X., Xu, W., Guo, J., Song, S., Qin, Y., Lin, P., Turner, J., Lee, H., Hwang, S., Liao, H., Martin, S., Zhang, Q., Chen, M., Sun, Y., Ge, X., and Jacob, D.: Fast sulfate formation from oxidation of SO_2 by NO_2 and HONO observed in Beijing haze, Nat. Commun., 11, 2844, https://doi.org/10.1038/s41467-020-16683-x, 2020.

6. Lines 215-225: The concluding paragraph is effective but could be strengthened by mentioning policy implications for sulfate control.

Response: We highly appreciate the reviewer's forward-looking suggestion, under the guidance of which we have substantially enriched the concluding remarks of the revised manuscript. By explicitly articulating the practical policy implications of our findings for regional sulfate mitigation, this updated section now effectively bridges our fundamental mechanistic insights with macro-level air quality management.

For more clarity, we have added/revised these sentences as following.

Page 17, Lines 302-312 in the revised manuscript:

By transcending the idealized SO_2 oxidation assumptions that constrain conventional isotopic models, this study offers a critical advancement in atmospheric sulfate source apportionment. Integrating field-observed oxidation kinetics with optimized fractionation corrections reveals the predominance of TMI-catalyzed and NO_2-mediated pathways-chemical realities that traditional complete-oxidation frameworks systematically obscure, thereby disproportionately diminishing TMI contributions and misallocating source-specific burdens. Crucially, correcting these systematic biases exposes a profound seasonal misalignment in current emission inventories, which overestimate coal combustion by 10% while underestimating traffic emissions by 8% during summer (Figure 6b). Beyond reconciling long-standing discrepancies among isotopic, inventory-based, and transport-modeling approaches, these refinements carry immediate policy implications. Specifically, they demonstrate

that effective sulfate mitigation cannot rely solely on blanket SO_2 reductions; rather, regulatory frameworks must pivot toward multi-pollutant, seasonally differentiated strategies that dynamically target summer traffic dynamics and the co-emitted transition metals driving catalytic sulfate formation.

7. Technical corrections: Line 28, remove the number "2".

Response: While apologizing for this initial omission, we have rectified the error by entirely omitting the numeral "2" throughout the updated manuscript.

For more clarity, we have added/revised these sentences as following.

Page 2, Lines 41-43 in the revised manuscript:

The application of stable isotope techniques in sulfate source attribution has emerged as a powerful analytical approach, leveraging the distinct isotopic fingerprints characteristic of different pollution sources and their remarkable stability during atmospheric transport.

8. Line 39: The sentence "Drawing conceptual inspiration from these insights" is vague.

Response: Appreciating the reviewer's thoughtful reminder, we have carefully recast the relevant formulations within the revised manuscript to ensure maximum clarity and scientific precision.

For more clarity, we have added/revised these sentences as following.

Page 2, Lines 49-58 in the revised manuscript:

Advanced analytical tools, particularly Bayesian isotopic mixing and Rayleigh fractionation models, have demonstrated substantial utility in deconvoluting complex sulfate formation mechanisms. Yet, their diagnostic potential is often overshadowed by a fundamental theoretical flaw: the reliance on complete SO_2 oxidation paradigms. Because genuine atmospheric regimes rarely achieve such idealized conversion, this oversimplification severely penalizes the accuracy of sulfur transformation kinetics. Ultimately, conventional Rayleigh approaches introduce systematic uncertainties into source apportionment by neglecting the vital kinetic isotope effects and partial intermediates generated during incomplete SO_2 processing.

Building upon these insights, the present study establishes a comprehensive multi-model analytical framework that synergistically couples ambient field observations

with a suite of diagnostic tools, ranging from backward trajectory analysis to Bayesian isotope mixing and process-specific Rayleigh fractionation modeling.

9. Line 43: Please change "sulfur-oxygen isotope analysis" to "sulfur and oxygen isotope analyses".

Response: We sincerely appreciate the reviewers' insightful suggestions for enhancing our manuscript. The "sulfur-oxygen isotope analysis" has been changed to "sulfur and oxygen isotope analyses".

For more clarity, we have added/revised these sentences as following.

Page 2, Lines 60-62 in the revised manuscript:

By applying sulfur and oxygen isotope analyses to seasonally resolved aerosol samples from Nanjing, we demonstrate significant divergence between conventional complete-oxidation Rayleigh models and our kinetic fractionation-corrected framework.

10. Line 58: Please remove "(08:00-08:00 local time)".

Response: We sincerely appreciate the reviewers' insightful suggestions for enhancing our manuscript. (08:00-08:00 local time)" has been deleted.

For more clarity, we have added/revised these sentences as following.

Page 3, Lines 76-77 in the revised manuscript:

Post-sampling handling included foil-wrapping (pre-combusted 723 K followed by 24-hour desiccation and dark refrigeration.

11. Line 60 and line 68: Please keep consistent with temperature units (450 ˚C V.S. 1073 K).

Response: We sincerely appreciate the reviewers' insightful suggestions for enhancing our manuscript. Line "450 ˚C" in line 60 has been changed to 723 K".

For more clarity, we have added/revised these sentences as following.

Page 3, Lines 73-77 in the revised manuscript:

Pre-treatment protocols involved muffle furnace combustion (723 K for 2h) followed by immersion in 2% K_2CO_3 + 2% glycerol solution for glass fiber filters. Sampling operations maintained 1.05 m^3 min^{-1} flow rates during 24-hour cycles with

meteorological parameters (wind speed/direction, temperature, pressure, humidity) continuously logged. Post-sampling handling included foil-wrapping (pre-combusted 723 K followed by 24-hour desiccation and dark refrigeration.

12. Line 191: Nanjing is in eastern China, not central. Please change "central China" to "eastern China".

Response: We sincerely appreciate the reviewers' insightful suggestions for enhancing our manuscript. "Central China" has been changed to "eastern China".

For more clarity, we have added/revised these sentences as following.

Page 15, Lines 273-275 in the revised manuscript:

An alternative α calculation (formula 9) generated a mean of 2.8 ± 1.7‰ (range: -0.2 to +6.1‰), higher than Guangzhou (<1.5‰) but lower than Beijing (4.2 ±1.2‰) with elevated α in eastern China attributable to temperature-dependent fractionation increases.

13. References:

Several references have incomplete DOIs (e.g., Han et al., 2022 has a PNAS DOI that doesn't match the journal)

Response: We sincerely appreciate the reviewers' insightful suggestions for improving the references. Han et al., 2022- the complete reference information has been supplemented.

Han, X., Lang, Y., Guo, Q., Li, X., Ding, H., and Li, S.: Enhanced oxidation of SO_2 by H_2O_2 during haze events: constraints from sulfur isotopes, J. Geophys. Res. Atmos., 127, e2022JD036960, https://doi.org/10.1029/2022JD036960, 2022.

For more clarity, we have added/revised these sentences as following.

Page 20, Lines 368-369 in the revised manuscript:

Han, X., Lang, Y., Guo, Q., Li, X., Ding, H., and Li, S.: Enhanced oxidation of SO_2 by H_2O_2 during haze events: constraints from sulfur isotopes, J. Geophys. Res. Atmos., 127, e2022JD036960, https://doi.org/10.1029/2022JD036960, 2022.

14. Mang et al., 2018- check author names

Response: We sincerely appreciate the reviewers' insightful suggestions for

improving the references. Lin, M., Zhang, X., Li, M., Xu, Y., Zhang, Z., Tao, J., Su, B., Liu, L., Shen, Y., and Thiemens, M. H.: Five-S-isotope evidence of two distinct mass-independent sulfur isotope effects and implications for the modern and Archean atmospheres, Proc. Natl. Acad. Sci., 115, 8541–8546, https://doi.org/10.1073/pnas.1803420115, 2018.

For more clarity, we have added/revised these sentences as following.

Page 20, Lines 394-396 in the revised manuscript:

Lin, M., Zhang, X., Li, M., Xu, Y., Zhang, Z., Tao, J., Su, B., Liu, L., Shen, Y., and Thiemens, M. H.: Five-S-isotope evidence of two distinct mass-independent sulfur isotope effects and implications for the modern and Archean atmospheres, Proc. Natl. Acad. Sci., 115, 8541–8546, https://doi.org/10.1073/pnas.1803420115, 2018.

15. Sinha, 2013 – incomplete reference (missing journal, volume, pages)

Response: We sincerely appreciate the reviewers' insightful suggestions for improving the references. Sinha, 2013-the complete reference information has been supplemented.

Harris, E., Sinha, B., Hoppe, P., and Ono, S.: High-precision measurements of ^{33}S and ^{34}S fractionation during SO_2 oxidation reveal causes of seasonality in SO_2 and sulfate isotopic composition, Environ. Sci. Technol., 47, 12174–12183, https://doi.org/10.1021/es402824c, 2013a.

For more clarity, we have added/revised these sentences as following.

Page 20, Lines 376-378 in the revised manuscript:

Harris, E., Sinha, B., Hoppe, P., and Ono, S.: High-precision measurements of ^{33}S and ^{34}S fractionation during SO_2 oxidation reveal causes of seasonality in SO_2 and sulfate isotopic composition, Environ. Sci. Technol., 47, 12174–12183, https://doi.org/10.1021/es402824c, 2013a.