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Advancing isotope-enabled model for comprehensive understanding of atmospheric sulfur isotope effects: demonstrating the overlooked isotopic fractionation during combustion and flue gas desulfurization

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This supporting information document contains 19 pages with detailed descriptions of CTM and model configuration, the algorithm framework of the isotopic chemistry module, the derivation of the stable isotopic composition of a reservoir in open systems, additional data, 2 tables, 3 figures, and references.

S1 The description of CTMs and model configuration. The three-dimensional atmospheric chemical transport model (CTMs) solves the continuity equation for the chemical species for representing its entire cycle in the atmosphere, including emission, transport (e.g. diffusion, advection), chemical production/loss, dry and wet deposition processes. The general Eulerian form of the continuity equation can be expressed mathematically by

$$\frac{\partial \bar{c}}{\partial t} = -\nabla \cdot (\bar{c}\bar{U}) + \nabla \cdot (K\nabla \cdot \bar{c}) + [\frac{\partial \bar{c}}{\partial t}]_{Emis} + [\frac{\partial \bar{c}}{\partial t}]_{Chem} - [\frac{\partial \bar{c}}{\partial t}]_{Dry} - [\frac{\partial \bar{c}}{\partial t}]_{Wet} \quad (S1)$$

where $\bar{c}$ is the time-averaged concentration of the chemical species of interest. The term on the left side is the temporal change of concentration. The first two terms on the right side are advection, and turbulent diffusion of the time-averaged flux, the last four terms represent the emission intensity, time-averaged rate of chemical interactions (including production and loss process), dry deposition, and wet scavenge. $\nabla = (\partial/\partial x, \partial/\partial y, \partial/\partial z)$ is the gradient vector, U = (u, v, w) is the local wind velocity vector, and K is a 3×3 matrix with zero values for the non-diagonal elements and with diagonal elements K_x, K_y, K_z representing the turbulent diffusion coefficients in each transport direction.

The model is initialized using gridded meteorological and emission input. The meteorological field is processed through the interpolation of NCEP FNL (Final) Operational Global Analysis and forecast dataset on 0.25° × 0.25° grids (2015), employing the WRF (Weather Research and Forecast model, version 3.9). Anthropogenic emissions, including SO_2, NO_x, NH_3, CO, VOCs, black carbon, and organic carbon, are obtained from the fusion of Hemispheric Transport of Air Pollution version-2 (HTAPv2) at a 1° horizontal resolution for the year 2010 (Janssens-Maenhout

et al., 2015), and the Multi-resolution Emission Inventory for China (MEIC) at a 0.1°× 0.1° horizontal resolution for the year 2015 (Li et al., 2017). The emission inventory for the Chinese region is overwritten with the MEIC. The online mineral dust is based on the wind erosion model developed by Wang et al. (2000) and the sea salt emissions parameterizations are referenced from Athanasopoulou et al. (2008), respectively.

The Rapid Radiative Transfer Model for General Circulation Model (RRTMG) scheme is employed for the computation of longwave and shortwave atmospheric radiative fluxes and heating rates (Pincus et al., 2003). The Madronich F-TUV (Fast Tropospheric Ultraviolet-Visible) scheme is utilized to estimate the photolysis rate. The WSM3 scheme (Hong et al., 2004) is selected for microphysics schemes. For the surface layer and boundary layer evaluations, the Monin-Obukhov scheme (Monin and Obukhov, 1954) and the Yonsei University (YSU) scheme (Hong et al., 2006) are chosen, respectively.

The Carbon Bond Mechanism version Z (CBM-Z) is employed for the gas-phase chemistry scheme (Zaveri and Peters, 1999). The aqueous chemistry module is taken from Regional Acid Deposition Model (RADM2) (Stockwell et al., 1997), including sulfur chemistry and a simple mechanism for wet scavenging. The dry deposition process is parameterized through the calculation of deposition velocity, employing the resistance model approach developed by Zhang et al. (2003). Recently, the Global Nested Grid Air Quality Prediction Model System (GNAQPMS) has been coupled with the CAS earth system model (CAS-ESM) (Wei et al., 2019). It shows good performance on the global budgets and spatial distribution of major atmospheric species, as validated against field observations and other model results. The oxidation processes of S(IV) to S(VI) involve gas-phase oxidation by SO_2 and OH radical, as well as aqueous phase oxidation

through dissoluble S(IV) with O_3, H_2O_2, NO_2, and proxy acetic acid (CH_3OOH), along with transition metal-catalyzed O_2 in cloud water. The oxidation of S(IV) species by dissolved NO_2 is also incorporated into the sulfur aqueous chemistry, referring to the kinetic parameters proposed by Cheng et al. (2016). The bulk cloud water pH is iteratively calculated online using the electroneutrality equation, considering concentrations of anions (sulfate, sulfite, nitrate, carbonate, formic acid) and cations (NH_4^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{3+}). Ion concentrations are determined based on Henry's law, dissociation equilibrium and ionization processes. Neutralized cations are mainly contributed by dust aerosol, with natural dust materials assumed to contain 10 wt% of Ca^{2+}, 3 wt% of Mg^{2+}, 0.5 wt% of Mn^{2+} and 0.5 wt% of Fe^{3+} (Wang et al., 2002). The gas–particle partitioning of inorganic aerosols and aerosol water content is simulated using the improved thermodynamic equilibrium module ISORROPIA II (Fountoukis and Nenes, 2007; Song et al., 2018). Refer to Table S2 for a comprehensive description of the model configuration.

The current implementation of the isotopic chemistry module relies on several assumptions. (1) The pollutants and cloud water are uniformly distributed within the grid cell. (2) During wet scavenging and dry deposition, no isotopic fractionation occurs, the small mass change due to isotopic substation is insignificant relative to the mass of particle, therefore, we apply the same K_j to ^{32}S and ^{34}S due to their similar molecular mass. (3) The model does not account for variations in isotopic composition from different emission sources. Instead, we focus on model's ability to reproduce the isotope effect, thus the isotopic composition of SO_2 and sulfate from emission sources are simply set to 0‰. The treatment does not influence the comparison between simulated and observed sulfur isotope effect during oxidation processes.

77

78 **S2 The algorithm framework of isotopic chemistry module**

79 We initially track the net change of SO_2 and sulfate after gas-phase, heterogeneous,
80 and cloud&aqueous chemistry module separately, and then determine the reaction
81 fraction *f* of SO_2 with each specific oxidation pathway during every time step (Δt) to be
82 used as input for the isotope chemistry module. At each time step, the temperature
83 and the temperature-dependent isotopic fractionation factor at the grid cell are
84 updated.

85 To reduce the effect of time-dependent Rayleigh equation with a large reaction
86 fraction. The iterative time-splitting technique is employed. Within each sub-timestep,
87 the reaction fraction is set at 2%, and a repetition involves adding equal portions of a
88 fresh mixture. Utilizing the input mass of sulfur-containing isotopologues $^{32}SO_2$ and
89 $^{34}SO_2$ at the last time step as initial value, we calculate the isotope ratio of $^{32}SO_4^{2-}$ and
90 $^{34}SO_4^{2-}$ in the product, as well as the isotope ratio of $^{32}SO_2$ and $^{34}SO_2$ in the remaining
91 reactant based on Rayleigh equations. We then derive the net mass change of $^{32}SO_2$,
92 $^{34}SO_2$, $^{32}SO_4^{2-}$ and $^{34}SO_4^{2-}$ using the isotopic mass balance at each sub-timestep, as
93 expressed in the following equation.

94 $$\Delta MC\left(\,^{l}X\right)_t = \left(MC\left(\,^{h}X\right)_{S,t-1} - R_{\mathrm{S},t} \times MC\left(\,^{l}X\right)_{S,t-1}\right)/\left(R_{P,t} - R_{\mathrm{S},t}\right) \quad \text{(S2)}$$

95 $$\Delta MC\left(\,^{h}X\right)_t = R_{\mathrm{S},t} \times \Delta MC\left(\,^{l}X\right)_t \quad \text{(S3)}$$

96 Where $\Delta MC\left(\,^{h}X\right)_t$ and $\Delta MC\left(\,^{l}X\right)_t$ represent the change in molar mass of
97 isotopologues containing heavier isotope ^{h}X and lighter isotope ^{l}X at time t during
98 the chemical process, respectively. $MC(\,^{h}X)_{S,t-1}$and $\mathrm{MC}(\,^{\mathrm{l}}\mathrm{X})_{\mathrm{S,t\text{-}1}}$ represent the molar
99 mass of reactant S containing heavier isotope ^{h}X and lighter isotope ^{l}X at time t-1,

respectively.

During each sub-timestep, the isotope ratio of the substrate is updated with the new mixing, and the isotope ratio of the accumulated product is weighted with the molar mass and isotope ratio of the product at each sub-timestep. An iterative loop is executed for the above steps.

S3 The derivation of stable isotopic composition of a reservoir in open systems.

We consider a reservoir that loses material due to any physicochemical process with isotopic fractionation at a constant temperature. At any instant, the stable isotope ratio is given by

$$R = \frac{N(\,^{h}X)}{N(\,^{l}X)} \qquad \text{(S4)}$$

where $N(\,^{h}X)$ and $N(\,^{l}X)$ represent the atomic abundances of the heavier stable isotope (^{h}X) and lighter stable isotope (^{l}X), respectively.

Taking the logarithm of both sides of Equation (S4)

$$lnR \;=\; ln\,N(\,^{h}X) - \;lnN(\,^{l}X) \quad \text{(S5)}$$

After differentiating, Equation (S5) becomes

$$\frac{dR}{R} = \frac{dN(\,^{h}X)}{N(\,^{h}X)} - \frac{dN(\,^{l}X)}{N(\,^{l}X)} = \frac{dN(\,^{h}X)}{N(\,^{l}X)\times R} - \frac{dN(\,^{l}X)}{N(\,^{l}X)} \qquad \text{(S6)}$$

At any instant, let $\mathrm{d}N(\,^{h}X)_{\mathrm{e}}$ and $\mathrm{d}N(\,^{l}X)_{\mathrm{e}}$ are being lost and $\mathrm{d}N(\,^{h}X)_{\mathrm{r}}$ and $\mathrm{d}N(\,^{l}X)_{\mathrm{r}}$ are being added to the reservoir. So, the net change in $N(\,^{h}X)$ and $N(\,^{l}X)$ is

$$dN(\,^{h}X) = \mathrm{d}N(\,^{h}X)_{\mathrm{r}} - \mathrm{d}N(\,^{h}X)_{\mathrm{e}} \quad \text{(S7)}$$

$$dN(\,^{l}X) = \mathrm{d}N(\,^{l}X)_{\mathrm{r}} - \mathrm{d}N(\,^{l}X)_{\mathrm{e}} \quad \text{(S8)}$$

Dividing Equation (S7) by Equation (S8)

$$\frac{dN(\,^{h}X)}{dN(\,^{l}X)} = \frac{\mathrm{d}N(\,^{h}X)_{\mathrm{r}} - \mathrm{d}N(\,^{h}X)_{\mathrm{e}}}{\mathrm{d}N(\,^{l}X)_{\mathrm{r}} - \mathrm{d}N(\,^{l}X)_{\mathrm{e}}} = \frac{\frac{\mathrm{d}N(\,^{h}X)_{\mathrm{r}}}{\mathrm{d}N(\,^{l}X)_{\mathrm{r}}}\times\frac{\mathrm{d}N(\,^{l}X)_{\mathrm{r}}}{\mathrm{d}N(\,^{l}X)_{\mathrm{e}}} - \frac{\mathrm{d}N(\,^{h}X)_{\mathrm{e}}}{\mathrm{d}N(\,^{l}X)_{\mathrm{e}}}}{\frac{\mathrm{d}N(\,^{l}X)_{\mathrm{r}}}{\mathrm{d}N(\,^{l}X)_{\mathrm{e}}} - 1} = \frac{\beta R_r - \alpha R}{\beta - 1} \qquad \text{(S9)}$$

Where α is defined as $(\mathrm{d}N(\,^{h}X)_{\mathrm{e}}/\mathrm{d}N(\,^{l}X)_{\mathrm{e}})/(N(\,^{h}X)/N(\,^{l}X))$, β is $\frac{\mathrm{d}N(\,^{l}X)_{\mathrm{r}}}{\mathrm{d}N(\,^{l}X)_{\mathrm{e}}}$, the ratio of the amount of material added to that lost, and R_r is the stable isotope ratio of the reactant added to the reservoir during the interval.

Substituting the value of $\mathrm{dN}(\,^{\mathrm{h}}\mathrm{X})$ from Equation (S9) to Equation (S6)

$$\frac{dR}{R} = \left(\frac{\beta R_r - \alpha R}{\beta - 1}\right) \times \frac{dN(\,^{l}X)}{N(\,^{l}X) \times R} - \frac{dN(\,^{l}X)}{N(\,^{l}X)} = \frac{dN(\,^{l}X)}{N(\,^{l}X)} \times \left(\frac{\beta \frac{R_r}{R}}{\beta - 1} - \frac{\alpha}{\beta - 1} - 1\right) \quad \text{(S10)}$$

or

$$\frac{dR}{\frac{\beta R_r}{\beta - 1} - \left(\frac{\alpha}{\beta - 1} + 1\right) \times R} = \frac{dN(\,^{l}X)}{N(\,^{l}X)} \quad \text{(S11)}$$

Taking integration on both sides, the integral on the left side is in the form of $\int \frac{1}{A - B \times R} dR$.

Using the substitution method, let $\mathrm{u} = \mathrm{A} - \mathrm{B} \times \mathrm{R}$, where $\mathrm{A} = \frac{\beta R_r}{\beta - 1}$, and $\mathrm{B} = \frac{\alpha}{\beta - 1} + 1$.

Differentiating with respect to R yield du = −B dR, so $\mathrm{dR} = -\frac{1}{B} du$. Substituting into the integral $\int \frac{1}{A - B \times R} dR$:

$$\int \frac{1}{u} \times \left(-\frac{1}{B}\right) du = -\frac{1}{B} \int \frac{1}{u} du = -\frac{1}{B} = -\frac{1}{B} \ln|A - B * R| \quad \text{(S12)}$$

Then substitute the previously defined A and B back into the formula to obtain the final complete solution. The condition for integrating this equation is

$$\frac{1}{-\left(\frac{\alpha}{\beta - 1} + 1\right)} \int \frac{d\left\{\frac{\beta R_r}{\beta - 1} - \left(\frac{\alpha}{\beta - 1} + 1\right) \times R\right\}}{\left\{\frac{\beta R_r}{\beta - 1} - \left(\frac{\alpha}{\beta - 1} + 1\right) \times R\right\}} = \int \frac{dN(\,^{l}X)}{N(\,^{l}X)} \quad \text{(S13)}$$

Where $\frac{\beta R_r}{\beta - 1} \neq \left(\frac{\alpha}{\beta - 1} + 1\right) \times R$, it gives that $\frac{dN(\,^{l}X)_r}{dN(\,^{l}X)_e} \neq \left(\frac{\alpha - 1}{\frac{R_r}{R} - 1}\right)$.

At β=1, this equation is not solvable, hence first we take the case where $\beta \neq 1$.

Case 1: on integrating Equation (S13), we get

$$\frac{1}{-(\frac{\alpha}{\beta-1}+1)} \times ln\left\{\frac{\beta R_r}{\beta-1} - (\frac{\alpha}{\beta-1} + 1) \times R\right\} = lnN(\ ^{l}X) + k \quad \text{(S14)}$$

After applying boundary conditions, at t_0, $N(\ ^{l}X)$=$N(\ ^{l}X)_0$, R=R_0, we evaluate *k* and substitute in Equation (S14); we get

$$\frac{1}{-(\frac{\alpha}{\beta-1}+1)} \times ln\left\{\frac{\frac{\beta R_r}{\beta-1} - (\frac{\alpha}{\beta-1}+1)\times R}{\frac{\beta R_r}{\beta-1} - (\frac{\alpha}{\beta-1}+1)\times R_0}\right\} = ln\frac{N(\ ^{l}X)}{N(\ ^{l}X)_0} = lnf_{rem} \quad \text{(S15)}$$

Here f_{rem} is the fraction of the material left in the reservoir relative to the initial amount.

Further simplifying Equation (S15) becomes

$$R = R_0 {f_{rem}}^{-(\frac{\alpha}{\beta-1}+1)} + \frac{\beta}{\alpha+\beta-1} \times R_r \times \left[1 - {f_{rem}}^{-(\frac{\alpha}{\beta-1}+1)}\right] \quad \text{(S16)}$$

or

$$R = R_0 {f_{rem}}^{\rho} + \frac{\beta}{\alpha+\beta-1} \times R_r \times [1 - {f_{rem}}^{\rho}] \quad \text{(S17)}$$

Here $\rho = -(\frac{\alpha}{\beta-1}+1)$.

Substituting β=0, Equation (S17) converts to the simple Rayleigh equation, which cross-checks the derivation.

$$R = R_0 {f_{rem}}^{(\alpha-1)} \quad \text{(S18)}$$

Case 2: When β=1, $\mathrm{d}N(\ ^{l}X) = 0$. Hence from Equation (S8),$\mathrm{d}N(\ ^{l}X)_\mathrm{r} = \mathrm{d}N(\ ^{l}X)_\mathrm{e}$. Equation (S6) becomes

$$dR = \frac{\mathrm{d}N(\ ^{h}X)_\mathrm{r} - \mathrm{d}N(\ ^{h}X)_\mathrm{e}}{N(\ ^{l}X)} = R_r \frac{\mathrm{d}N(\ ^{l}X)_\mathrm{r}}{N(\ ^{l}X)} - \alpha R \frac{\mathrm{d}N(\ ^{l}X)_\mathrm{e}}{N(\ ^{l}X)}$$

$$= (\frac{R_r - \alpha R}{N(\ ^{l}X)})dN(\ ^{l}X)_r = (\frac{R_r - \alpha R}{N(\ ^{l}X)_0})dN(\ ^{l}X)_r \quad \text{(S19)}$$

After rearranging and integrating, this becomes

160 $$-\frac{1}{\alpha}\int\frac{d(R_r-\alpha R)}{R_r-\alpha R}=\frac{1}{N(\ ^lX)_0}\int dN(\ ^lX)_r \quad \text{(S20)}$$

161 After solving fully and applying boundary conditions as in the previous case, we get

162 $$R=R_0 exp\left[-\frac{\alpha N(\ ^lX)_r}{N(\ ^lX)_0}\right]+(R_r/\alpha)\times\left\{1-exp\left[-\frac{\alpha N(\ ^lX)_r}{N(\ ^lX)_0}\right]\right\} \quad \text{(S21)}$$

163 Here $N(\ ^lX)_r$ indicates the total number of lighter isotopic molecules added thus far.

Table S1 Compiled observation data of $\delta^{34}S$ values of coal, sulfate aerosol, and wet precipitation across different Chinese provinces

Province	$\delta^{34}S$ of coal	$\delta^{34}S$ of wet precipitation	$\delta^{34}S$ of aerosol
Beijing	7.4±16.1	4.7±1.8	6.1±1.3
Tianjin			4.1±1.6
Inner Mongolia	0.8		
Heilongjiang	3.2±1.8		6.4
Liaoning	9.4±3.2		5.9
Jilin	1.7		8.1
Hebei	3.5±6.6		
Henan	6.4±1.0	2.1±2.3	
Shandong	7.6±2.9		
Gansu	7.3±3.5		
Zhejiang	4.0±1.5		6.2±2.7
Jiangsu	3.8±1.3		5.5±1.0
Anhui	3.8		
Fujian			3.5±1.1
Chongqing		4.3±1.1	
Jiangxi	-4.4±1.3		
Sichuan	8.8±1.3	3.9	
Shaanxi	7.9±4.6	12.3±1.1	
Shanxi	12.1±10.8		
Hubei	12.1		
Hunan	-6.6±5.7		
Guangdong	9.6±1.0		5.2±1.6
Guizhou	-7.5±0.1	-2.8±9.8	1.2
Yunnan	-0.7		

The dataset (Mean±std.) is compiled from references.

The compiled data from various Chinese provinces are cited from sources such as Beijing (Fan et al., 2020; Wei et al., 2018; Han et al., 2016b; Hong et al., 1993; Maruyama et al., 2000; Ohizumi et al., 1997; Mukai et al., 2001; Han et al., 2016a; Zhu et al., 2016), Tianjin (Han et al., 2022; Ding et al., 2022), Inner Mongolia (Hong et al., 1993), Heilongjiang (Hong et al., 1993; Ohizumi et al., 1997; Mukai et al., 2001), Liaoning (Hong et al., 1993; Maruyama et al., 2000; Ohizumi et al., 1997), Jilin

(Hong et al., 1993; Mukai et al., 2001), Hebei (Hong et al., 1993), Henan (Hong et al., 1993; Zheng et al., 2024), Shandong (Hong et al., 1993), Gansu (Xiao and Liu, 2011), Zhejiang (Hong et al., 1993; Lin et al., 2022), Jiangsu (Hong et al., 1993; Chen et al., 2017; Li et al., 2020; Maruyama et al., 2000; Mukai et al., 2001), Anhui (Hong et al., 1993), Fujian (Lin et al., 2018), Chongqing (Xiao et al., 2009; Wu and Han, 2015), Jiangxi (Hong et al., 1993; Xiao and Liu, 2011; Xiao et al., 2009), Sichuan (Hong et al., 1993; Xiao et al., 2009), Shaanxi (Xiao and Liu, 2011; Bai and Wang, 2014), Shanxi (Xiao and Liu, 2011; Maruyama et al., 2000; Ohizumi et al., 1997), Hubei (Xiao and Liu, 2011), Hunan (Hong et al., 1993; Xiao and Liu, 2011), Guangdong (Lin et al., 2018), Guizhou (Hong et al., 1993; Mukai et al., 2001; Xiao et al., 2009; Xiao et al., 2014), Yunnan (Hong et al., 1993)

182 **Table S2 The detailed information of model configurations**

Module	Parameterizations/schemes
Input global analysis data	NCEP GDAS/FNL data
Gas-phase chemical mechanism	CBM-Z mechanism (Zaveri and Peters, 1999)
Aqueous-phase chemical mechanism and wet scavenge	RADM mechanism (Chang et al., 1987)
Anthropogenic emissions	HTAPv2 and MEIC
Dust, sea salt	wind erosion model (Wang et al., 2000) sea salt online parameterization (Athanasopoulou et al., 2008)
Photolysis scheme	Madronich F-TUV
Microphysics scheme	WSM3 (Hong et al., 2004)
Longwave radiation scheme	RRTM (Mlawer et al., 1997)
Shortwave radiation scheme	Dudhia scheme (Dudhia, 1989)
Surface layer	Monin-Obukhov (Janjic) scheme (Monin and Obukhov, 1954)
Land surface schemes	NOAH (Ek et al., 2003)
Planetary boundary layer physics	YSU scheme (Hong et al., 2006)
Cumulus	Kain-Fritsch scheme (Kain, 2004)
Vertical layers	20

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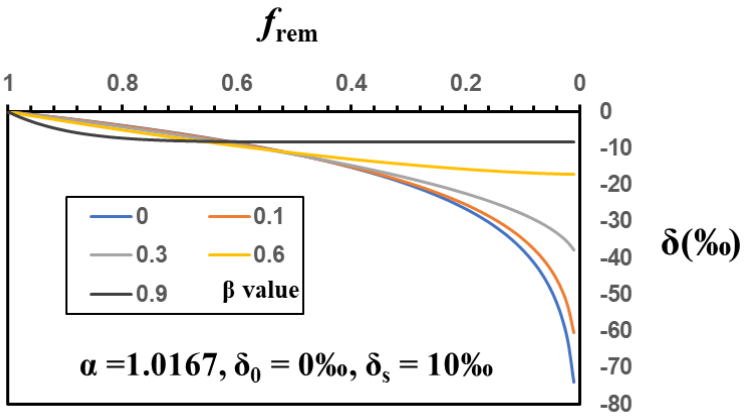
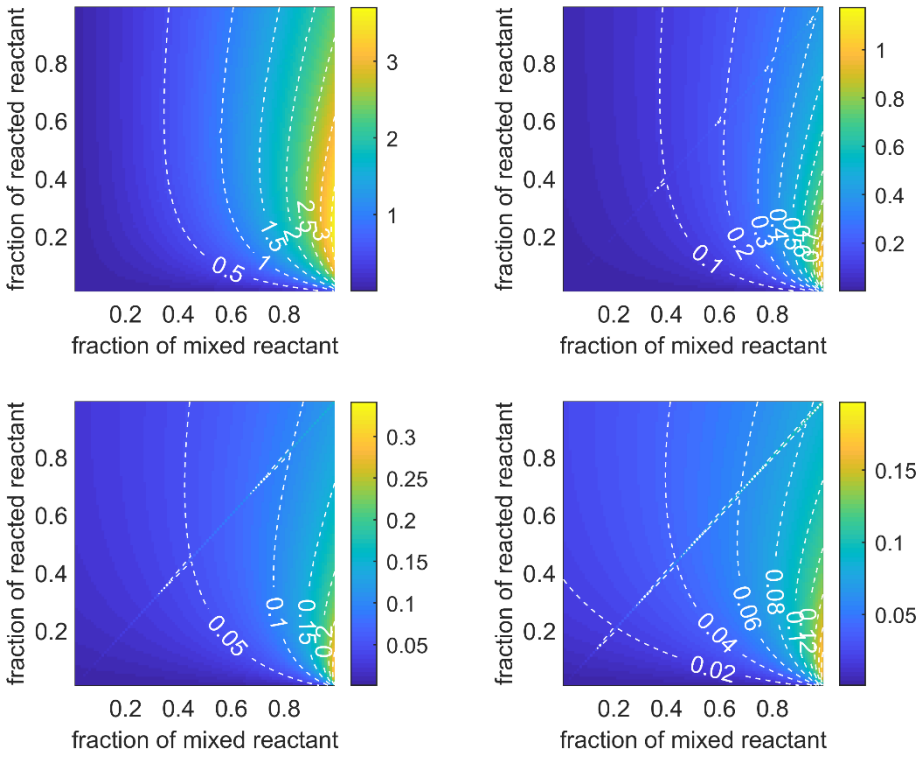


Figure S1. An example illustrating the change in isotopic composition (δ) of a reservoir related to the remaining fraction (f_{rem}) of the original material, considering various values of β, which represents the ratio of the instantaneous amount added to the removal during an infinitesimal time interval Δt ($\beta \neq 1$). The isotopic composition of the external source (δ_s) is assumed to be 10‰, and the fractionation factor is set to 1.0167.



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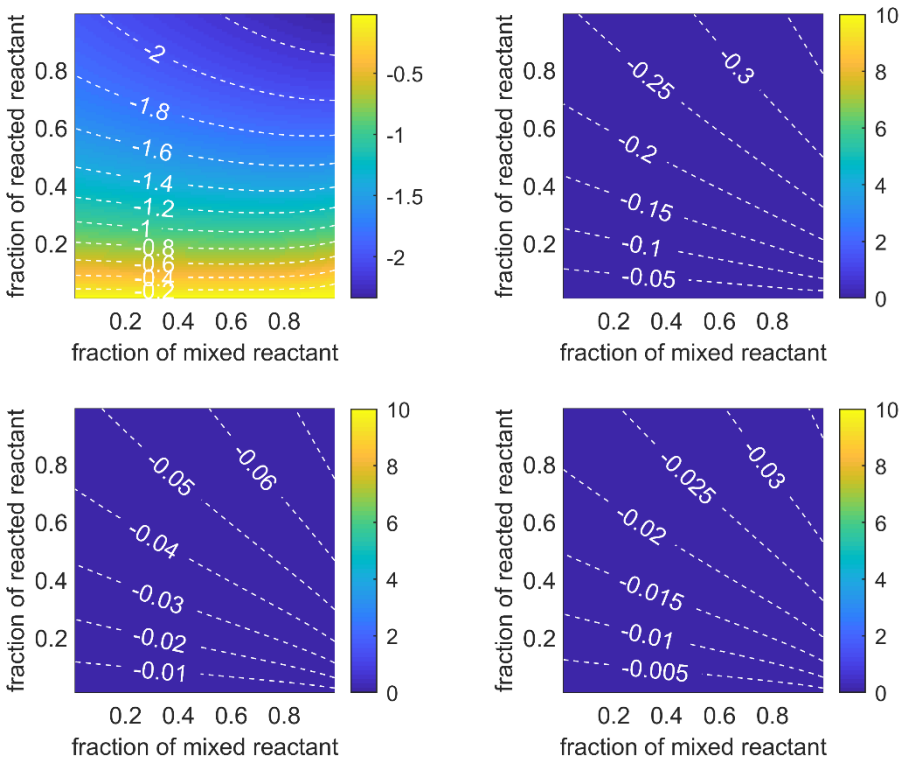
195 **Figure S2**. Simulation deviation of the isotopic composition of reservoir for varying
196 sub-steps (a) 1, (b) 10, (c) 50, and (d) 100, relative to reference simulation with
197 integration method in the open system associated with simultaneous reaction and
198 mixing processes. Each simulation involves the addition of a compound with an initial
199 δ-value of 10.0‰ to the substrate (initially δ= 0‰), while the chemical reaction
200 exhibits an isotopic effect with a fractionation factor of α= 1.0167. The fractions of
201 added and removed products range from 1% to 99% of the initial amount of substrate
202 and are uniformly divided at every time sub-step. The color scheme and contour lines
203 illustrate the δ-value differences between the respective simulations and the
204 referenced simulation.

205



206

207 **Figure S3.** Simulation deviation of the isotopic composition of the product for varying
208 sub-steps (a) 1, (b) 10, (c) 50, and (d) 100, relative to reference simulation with 1000
209 sub-steps. Each simulation involves the addition of a compound with an initial δ-value
210 of 10.0‰ to the substrate (initially δ = 0‰), while the chemical reaction exhibits an
211 isotopic effect with a fractionation factor of α= 1.0167. The fractions of added and
212 removed products range from 1% to 99% of the initial amount of substrate and are
213 uniformly divided at every time sub-step. The color scheme and contour lines illustrate
214 the δ-value differences between the respective simulations and the referenced
215 simulation.

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