

# Stable Sulfur Isotopes Revealed a Major Role of Transition-Metal Ion-Catalyzed SO<sub>2</sub> Oxidation in Haze Episodes

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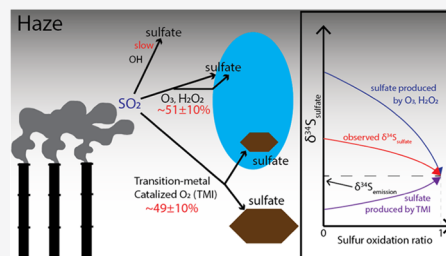
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**ABSTRACT:** Secondary sulfate aerosols played an important role in aerosol formation and aging processes, especially during haze episodes in China. Secondary sulfate was formed via atmospheric oxidation of SO<sub>2</sub> by OH, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and transition-metal-catalyzed (TMI) O<sub>2</sub>. However, the relative importance of these oxidants in haze episodes was strongly debated. Here, we use stable sulfur isotopes ( $\delta^{34}\text{S}$ ) of sulfate aerosols and a Rayleigh distillation model to quantify the contributions of each oxidant during a haze episode in Nanjing, a megacity in China. The observed  $\delta^{34}\text{S}$  values of sulfate aerosols showed a negative correlation with sulfur oxidation ratios, which was attributed to the sulfur isotopic fractionations during the sulfate formation processes. Using the average fractionation factor calculated from our observations and zero-dimensional (0-D) atmospheric chemistry modeling estimations, we suggest that OH oxidation was trivial during the haze episode, while the TMI pathway contributed  $49 \pm 10\%$  of the total sulfate production and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> oxidations accounted for the rest. Our results displayed good agreement with several atmospheric chemistry models that carry aqueous and heterogeneous TMI oxidation pathways, suggesting the role of the TMI pathway was significant during haze episodes.



## INTRODUCTION

Haze episodes in Chinese cities are adversely affecting the environment and the health of millions of residents. Most haze episodes are characterized by high concentrations and fast accumulation of aerosol sulfate,<sup>1–4</sup> which could contribute to as much as 45% of the total aerosol mass. Over 90% sulfate in haze episodes is the secondary sulfate, i.e., the sulfate produced from SO<sub>2</sub> oxidation in the atmosphere via (1) gas-phase oxidation by OH radical;<sup>5</sup> (2) aqueous oxidation by H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, and transition-metal ion (TMI)-catalyzed O<sub>2</sub>;<sup>6–12</sup> and (3) heterogeneous oxidation on the surface of aerosols, cloud droplets, and mineral dusts by the same oxidants as aqueous oxidation.<sup>1,13–16</sup> Some studies<sup>11,12,14,17,18</sup> also suggested that NO<sub>2</sub> might play an important role during the formation of the aerosol sulfate, probably by facilitating TMI oxidation,<sup>19</sup> which is based on an experimental study<sup>20</sup> that demonstrated that the direct oxidation of SO<sub>2</sub> by NO<sub>2</sub> was several orders of magnitude slower than gas-phase OH oxidation. However, aerosol collected from several Chinese urban areas (e.g., Nanjing) was acidic,<sup>21</sup> suggesting that NO<sub>2</sub> oxidation might not be important in these regions. Furthermore, a recent GEOS-Chem modeling study<sup>22</sup> has suggested that NO<sub>2</sub> oxidation contributed less than 2% of total sulfate production during haze episodes. While the gas-phase oxidation rate of SO<sub>2</sub> + OH is well-constrained, there are many uncertainties in quantifying the rates of aqueous and heterogeneous SO<sub>2</sub> oxidation. One of the ongoing debates is the relative contribution of each SO<sub>2</sub> oxidation pathway during haze episodes. Some<sup>8,12,13</sup> have suggested that O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>

oxidation of SO<sub>2</sub> in the aqueous phase contributed to the majority of total sulfate production, while the TMI pathway played a minor role. Others<sup>17,23</sup> have countered that the TMI pathway is likely also very important in highly polluted regions. Therefore, addressing this debate is essential to unravel the complex atmospheric sulfur chemistry in haze episodes.

Atmospheric chemistry models are often used to study the sulfate chemistry, but many models have uncertainties in parameterizing aqueous and heterogeneous SO<sub>2</sub> oxidation chemistry under haze conditions, resulting in underestimation of sulfate formation rates during haze episodes.<sup>1,24–26</sup> One of the biggest uncertainties is the pH of aerosol water; several studies had attempted to calculate the aerosol water pH in Beijing<sup>12,17,27–29</sup> using the same model (ISORROPIA II). Depending on assumptions about whether the aqueous phase is at the thermodynamic stable state,<sup>17,30</sup> the calculated pH was either 3–5 or >5.5. This uncertainty greatly impacts the quantification of the aqueous SO<sub>2</sub> oxidation rate.<sup>31</sup> A pH increase of 1 unit will increase the O<sub>3</sub> oxidation rate by 2 orders of magnitude but decrease the TMI oxidation rate by 2–3 orders of magnitude. Conversely, the rate of SO<sub>2</sub> oxidation by H<sub>2</sub>O<sub>2</sub> is insensitive to the changing pH. Additionally, atmospheric models usually quantify the rate of

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the TMI oxidation pathway using modeled aerosol Fe and Mn concentrations.<sup>10</sup> However, studies<sup>9,32</sup> have suggested that aerosol surface type, temperature, irradiation, and the existence of other transition metals in aerosol water could alter the rate of TMI oxidation by as much as 2 orders of magnitude, adding more complexity to this question. Therefore, to (1) reduce the uncertainties in atmospheric models and (2) verify the performance in models during haze episodes, an alternative approach is needed to assess the relative importance of each oxidation pathway.

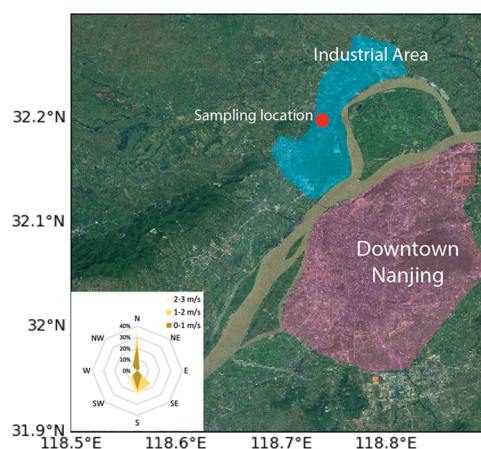
The isotopic composition of sulfate aerosols has been used to determine the formation processes of sulfate aerosols. The mass-independent fractionation signals (nonzero  $\Delta^{17}\text{O}$ , where  $\Delta^{17}\text{O} = \delta^{18}\text{O} - 0.52 \times \delta^{17}\text{O}$ ) of oxygen isotopes in sulfates are often used to estimate the contributions of  $\text{SO}_2 + \text{O}_3$  and  $\text{H}_2\text{O}_2$  to the formation of sulfate aerosols,<sup>10,17,33</sup> since  $\text{SO}_2 + \text{O}_3$  and  $\text{SO}_2 + \text{H}_2\text{O}_2$  are the only known two pathways that produce nonzero  $\Delta^{17}\text{O}$  values in sulfates.<sup>34</sup> The sulfate formed via  $\text{SO}_2 + \text{O}_3$  yields  $\Delta^{17}\text{O} = 6.5\text{‰}$ , and the sulfate formed via  $\text{SO}_2 + \text{H}_2\text{O}_2$  shows  $\Delta^{17}\text{O} = 0.7\text{‰}$ . This method can easily identify the significant contribution of the  $\text{SO}_2 + \text{O}_3$  pathway when high  $\Delta^{17}\text{O}$  ( $>3\text{‰}$ ) is measured in sulfate samples. There is significant uncertainty, however, when interpreting sulfate aerosols with low  $\Delta^{17}\text{O}$  values ( $<1\text{‰}$ ). Unfortunately, most sulfate aerosols in haze episodes show  $\Delta^{17}\text{O} < 1\text{‰}$ ,<sup>17,22</sup> suggesting a limited contribution from the  $\text{SO}_2 + \text{O}_3$  pathway but the relative importance of the  $\text{SO}_2 + \text{H}_2\text{O}_2$  pathway and the TMI pathway is still unclear. Therefore, solely using  $\Delta^{17}\text{O}$  probably cannot precisely distinguish the contributions from the  $\text{SO}_2 + \text{H}_2\text{O}_2$  and the TMI pathways in haze episodes.

Stable sulfur isotopes ( $\delta^{34}\text{S}$ ) have the potential to indicate the formation pathways of sulfate aerosols. The fractionation factors for sulfur isotopes during multiple oxidation pathways ( $\text{SO}_2 + \text{OH}$ ,  $\text{SO}_2 + \text{H}_2\text{O}_2/\text{O}_3$ , and TMI) have been determined experimentally.<sup>35–37</sup> Yet, to date, there are few studies using sulfate  $\delta^{34}\text{S}$  values to interpret the oxidation pathways of  $\text{SO}_2$ .<sup>35,38,39</sup> This is because the  $\delta^{34}\text{S}$  values of sulfate aerosols ( $\delta^{34}\text{S}_{\text{sulfate}}$ ) are simultaneously controlled by the  $\delta^{34}\text{S}$  values of  $\text{SO}_2$  sources<sup>40,41</sup> ( $\delta^{34}\text{S}_{\text{emission}}$ ) and the kinetic and equilibrium isotope effects occurring during the oxidation process. The  $\delta^{34}\text{S}_{\text{emission}}$  values strongly depend on the origin of  $\text{SO}_2$  and can, therefore, be difficult to constrain. However, during haze episodes,  $\text{SO}_2$  generally originates from local sources because air stagnation limits long-range transport and the  $\delta^{34}\text{S}_{\text{emission}}$  values can be well-constrained using local  $\text{SO}_2$  emission inventory and observations. Thus, the differences between  $\delta^{34}\text{S}_{\text{emission}}$  and  $\delta^{34}\text{S}_{\text{sulfate}}$  can be attributed to the isotopic fractionations during the oxidation processes, which are controlled by the oxidation pathways. This isotopic fractionation during  $\text{SO}_2$  oxidation should be treated as a Rayleigh distillation process<sup>42</sup> since isotopic exchange between the product sulfate and the reactant  $\text{SO}_2$  is minimal.<sup>35</sup> Currently, many studies have measured  $\delta^{34}\text{S}_{\text{sulfate}}$  in Chinese megacities<sup>38,39,43–47</sup> to understand the sources of atmospheric  $\text{SO}_2$  and the secondary sulfate aerosols. Some works also have measured  $\delta^{33}\text{S}$  and  $\delta^{36}\text{S}$ <sup>47–51</sup> to further constrain the origins of atmospheric  $\text{SO}_2$ . However, the differences between  $\delta^{34}\text{S}_{\text{emission}}$  and  $\delta^{34}\text{S}_{\text{sulfate}}$  as well as the isotopic fractionation process during the formation of sulfate, were rarely discussed and poorly understood. Here, we used the Rayleigh distillation model to investigate the sulfur isotopic fractionations of sulfate aerosols collected during a haze episode in winter 2015 at

Nanjing, China, to understand the relative contribution of each  $\text{SO}_2$  oxidation pathway.

## MATERIALS AND METHODS

Sulfate aerosols were sampled during a severe haze episode in winter 2015, in Nanjing, People's Republic of China. The sampling site was located at the Agrometeorological station in Nanjing University of Information Science and Technology (NUIST). Two large industrial areas are located  $\sim 10$  km northeast and  $\sim 5$  km southwest of the sampling site, and downtown Nanjing is 20 km to the southeast (Figure 1). A



**Figure 1.** Sampling location was in between two large industrial areas (blue) and downtown Nanjing (red) is 20 km to the southeast. Wind rose during the sampling period is shown at the lower-left corner; the highest 3 h wind speed was  $< 3$  m/s, indicating air stagnation.

high-volume aerosol sampler equipped with a precombusted quartz filter was used to collect ambient aerosol samples ( $< 2.5 \mu\text{m}$  in diameter,  $\text{PM}_{2.5}$ ) from January 22nd to 28th at a flow rate of  $1 \text{ m}^3/\text{min}$ , and the filter was replaced every 3 h. Once the aerosol samples were collected, the filters were wrapped in an aluminum foil, sealed in air-tight polyethylene bags, and stored in a freezer to minimize sample loss or evaporation. To determine the anion and cation concentrations of filter samples, a quarter of each filter was cut and the soluble components on the filter were dissolved into 50 mL of Millipore water ( $18.2 \text{ M}\Omega$ ). Then, the solution was sonicated for at least 30 min to ensure all of the soluble ions were completely dissolved. Subsequently, the solutions were filtered through  $0.45 \mu\text{m}$  filters to remove insoluble materials. An aliquot of each solution was taken and was used to measure the anion and cation concentrations using a Dionex ICS 5000+ at NUIST following the standard ion chromatography (IC) procedure,<sup>52</sup> while the rest of the solutions were kept frozen. The analytical uncertainty for the IC analysis was  $\pm 5\%$ . Meteorological data (wind speed and direction, temperature, and RH) were obtained from an automatic meteorological station next to the sampling site. Concentrations of pollutants ( $\text{PM}_{2.5}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{O}_3$ ,  $\text{CO}$ , and  $\text{SO}_2$ ) were obtained from the environmental supervising station at Pukou District, Nanjing,  $\sim 15$  km away from the sampling site.

The sulfur isotopic analysis was conducted at the Purdue Stable Isotope Laboratory at the Purdue University. The sulfur isotopic analysis follows the procedure by Li et al.<sup>40</sup> Another quarter of each sample was again dissolved into 10 mL of Millipore water ( $18.2 \text{ M}\Omega$ ), and each solution was sonicated

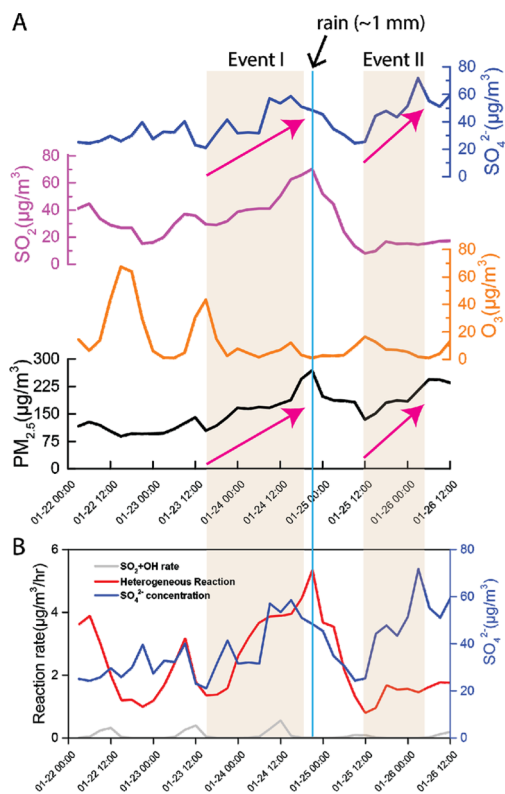
for 30 min to completely dissolve all of the sulfates on the filter. To completely precipitate  $\text{BaSO}_4$ , 1 mL of 5%  $\text{BaCl}_2$  solution and subsequently 0.5 mL of 37% HCl were added into each sample solution. Between 0.1 and 0.5 mg of the  $\text{BaSO}_4$  precipitate was then weighed into tin boats and combusted at 980 °C in an elemental analyzer (Costec), and then the product  $\text{SO}_2$  was directed into an isotope ratio mass spectrometer (ThermoDeltaV) to measure the  $\delta^{34}\text{S}$  values. The analytical uncertainty of the sulfur isotopic analysis was  $\pm 0.1\%$ , inferred from IAEA-SO5 and IAEA-SO6 external standards.

## RESULTS AND DISCUSSION

The haze episode occurred in Nanjing during winter 2015 and was characterized by high  $\text{PM}_{2.5}$ , high sulfate concentrations, and air stagnation. Prior to the haze episode (between January 18 and 21, 2015), the  $\text{PM}_{2.5}$  concentrations averaged  $83.1 \mu\text{g}/\text{m}^3$ . The haze episode began between January 22, 00:00 and January 23, 12:00 when  $\text{PM}_{2.5}$  increased, with concentrations of  $109.3 \pm 16.0 \mu\text{g}/\text{m}^3$ .  $\text{PM}_{2.5}$  continued to increase to an average of  $159.4 \mu\text{g}/\text{m}^3$  between the 22nd and 26th of January during which two significant  $\text{PM}_{2.5}$  accumulation events were observed. The first accumulation (Event I, Figure 2A) started on January 23, 13:30 and lasted for 33 h, during which the  $\text{PM}_{2.5}$  concentration more than doubled, from 104.0 to  $268.3 \mu\text{g}/\text{m}^3$ . This was followed by a 2 h light precipitation ( $\sim 1$  mm), which rinsed out some of the  $\text{PM}_{2.5}$ , decreasing its concentration to  $134.0 \mu\text{g}/\text{m}^3$  within 15 h. A subsequent  $\text{PM}_{2.5}$

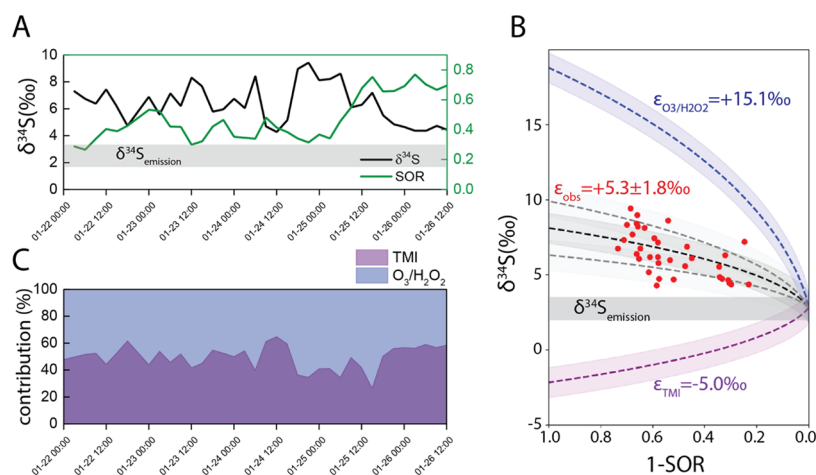
accumulation period (Event II) occurred within 24 h, when the  $\text{PM}_{2.5}$  concentration increased from 134.0 to  $243.7 \mu\text{g}/\text{m}^3$ . Sulfate aerosol concentrations followed trends similar to  $\text{PM}_{2.5}$  concentrations and mirrored the two rapid accumulation events. During Event I, sulfates have increased from 21.0 to  $58.5 \mu\text{g}/\text{m}^3$  in 27 h (an accumulation rate of  $1.39 \mu\text{g}/\text{m}^3/\text{h}$ ), and during Event II, sulfates have increased from 24.4 to  $71.8 \mu\text{g}/\text{m}^3$  within 21 h (an accumulation rate of  $2.26 \mu\text{g}/\text{m}^3/\text{h}$ ). Primary sulfate (includes the soil sulfate, the sea-salt sulfate, and the sulfate directly emitted with  $\text{SO}_2$ ) was determined to be trivial during these events. Low concentrations of  $\text{Ca}^{2+}$  ( $1.88 \pm 1.09 \mu\text{g}/\text{m}^3$ ) and  $\text{Na}^+$  ( $0.97 \pm 0.86 \mu\text{g}/\text{m}^3$ ) in the aerosols indicated that contribution of sulfates from soil entrainment<sup>53</sup> ( $\text{SO}_4^{2-}/\text{Ca}^{2+} = 0.18$ ) and sea-salt aerosols<sup>54</sup> ( $\text{SO}_4^{2-}/\text{Na}^+ = 0.25$ ) should be less than  $0.58 \mu\text{g}/\text{m}^3$ , corresponding to  $<2\%$  of the total sulfate observed. The primary sulfate emitted with  $\text{SO}_2$  during coal burning has been estimated to be only  $<4\%$  of  $\text{SO}_2$  emission,<sup>10,55</sup> which based on observed  $\text{SO}_2$  concentrations, would average at  $1.66 \pm 0.6 \mu\text{g}/\text{m}^3$  during the sampling period (Figure 2A). Thus, the total primary sulfate only contributed for  $<6\%$  of the total sulfate, indicating that most were the secondary sulfate (i.e.,  $\text{SO}_2$  oxidation). Additionally, the wind speed during the entire haze episode averaged at  $1.03 \pm 0.71$  m/s with a maximum 3 h wind speed of 2.58 m/s (wind rose in Figure 1), indicating air stagnation. Considering the short lifetime<sup>31</sup> of atmospheric  $\text{SO}_2$  ( $\sim 12$  h) and aerosols ( $\sim 5$  days) and the relatively low sulfur emissions outside of Nanjing within 200 km inferred from  $\text{SO}_2$  emission inventory,<sup>56</sup> long-range transportation of  $\text{SO}_{2(\text{g})}$  and sulfates should be minor; thus, local  $\text{SO}_2$  emissions and oxidation within Nanjing should be the dominant source of aerosol sulfate.

The measured  $\delta^{34}\text{S}_{\text{sulfate}}$  values were significantly higher than the estimated  $\delta^{34}\text{S}_{\text{emission}}$  values in Nanjing,<sup>38,39,44</sup> showing a  $\sim 5\%$  variation throughout the sampling period and displayed a negative correlation with the  $\text{SO}_2$  oxidation ratio ( $\text{SOR} = \text{SO}_4^{2-}/(\text{SO}_4^{2-} + \text{SO}_2)$ ).  $\delta^{34}\text{S}_{\text{sulfate}}$  values (Figure 3A) in our samples ranged from  $+4.3$  to  $+9.4\%$  with an average of  $6.2\%$ , similar to the values observed in a number of other Chinese megacities.<sup>23,44–46</sup> Because of air stagnation,  $\text{SO}_2$  likely originated from local emissions, the majority of which in Nanjing was coal combustion with a  $\delta^{34}\text{S}$  value of  $3.0 \pm 0.9\%$ .<sup>43</sup> Several studies have measured the  $\delta^{34}\text{S}$  values of both  $\text{SO}_2$  and sulfates simultaneously at Nanjing, showing that the  $\delta^{34}\text{S}_{\text{emission}}$  ( $\delta^{34}\text{S}_{\text{emission}} = \delta^{34}\text{S}_{\text{SO}_2} \times (1 - \text{SOR}) + \delta^{34}\text{S}_{\text{SO}_4^{2-}} \times \text{SOR}$ ) was  $+4.0 \pm 0.1\%$ <sup>44</sup> in 1997 and  $2.4 \pm 0.6\%$ <sup>38</sup> in fall 2014. Chen et al.<sup>39</sup> have analyzed the  $\delta^{34}\text{S}_{\text{emission}}$  in Nanjing prior to our sampling period (daily  $\text{SO}_2$  and sulfate samples from January 1 to 23, while this work sampled 3 h sulfate samples from January 22 to 26) and found a constant  $\delta^{34}\text{S}_{\text{emission}}$  value of  $2.7 \pm 1.0\%$ .<sup>39</sup> Therefore, we suggest that the  $\delta^{34}\text{S}_{\text{emission}}$  value during our sampling period should also be  $2.7 \pm 1.0\%$  (Figure 3A). These values are in good agreement with the  $\text{SO}_2$  emission inventory,<sup>56</sup> which suggested that over 96%  $\text{SO}_2$  emission in winter in the Nanjing area was from industrial and coal-burning power plants, which had a  $\delta^{34}\text{S}$  value of  $3 \pm 3\%$ .<sup>44,57</sup> The measured  $\delta^{34}\text{S}_{\text{sulfate}}$  values were significantly higher than the  $\delta^{34}\text{S}_{\text{emission}}$ , suggesting enrichment of  $^{34}\text{S}$  in the sulfate and hence a depletion of  $^{34}\text{S}$  in the remaining  $\text{SO}_2$ . This phenomenon has been observed in other studies, where the  $\delta^{34}\text{S}$  values of the aerosol sulfate were usually 0–8% higher than the coexisting  $\text{SO}_2$ <sup>38,39,41,44,58,59</sup> but



**Figure 2.** (A) Concentrations of sulfates,  $\text{SO}_2$ ,  $\text{O}_3$ , and  $\text{PM}_{2.5}$  during the haze episode. Shaded areas indicated two rapid  $\text{PM}_{2.5}$  and sulfate accumulation events, and the blue line indicated a small rain event during the sampling period; (B) calculated reaction rates of  $\text{SO}_2 + \text{OH}$  (gray) and heterogeneous reaction (red) plotted with sulfate concentrations (blue).





**Figure 3.** (A) Measured  $\delta^{34}\text{S}_{\text{sulfate}}$  (black) and the calculated sulfur oxidation ratio (SOR, green) throughout the sampling period and compared with the estimated  $\delta^{34}\text{S}_{\text{emission}}$  (gray bar); (B) Rayleigh distillation model of sulfate production. The gray bar indicates the  $\delta^{34}\text{S}_{\text{emission}}$  ( $+2.7 \pm 1.0\text{‰}$ ) in Nanjing, red circles are the measured  $\delta^{34}\text{S}_{\text{sulfate}}$  value in this study. Dashed lines with shaded areas are calculated  $\delta^{34}\text{S}_{\text{sulfate}}$  values based on the  $\delta^{34}\text{S}_{\text{emission}}$ ; the blue line indicates the  $\delta^{34}\text{S}_{\text{sulfate}}$  value when  $\text{SO}_2$  is oxidized solely by  $\text{O}_3$  and  $\text{H}_2\text{O}_2$ , the purple line indicates the  $\delta^{34}\text{S}_{\text{sulfate}}$  value when  $\text{SO}_2$  is oxidized solely by TMI oxidation, the black line is the estimated  $\epsilon$  value of  $+5.3\text{‰}$ , and two gray lines represent the upper and lower limits for the estimated  $\epsilon$  values ( $+3.5$  and  $+7.1\text{‰}$ ). (C) Relative contributions of TMI and  $\text{O}_3/\text{H}_2\text{O}_2$  oxidations during the sampling period.

this phenomenon was not quantitatively explained. Also, the  $\delta^{34}\text{S}_{\text{sulfate}}$  values showed a  $\sim 5.1\text{‰}$  variation throughout the sampling period. If the  $\delta^{34}\text{S}_{\text{emission}}$  remains constant during our sampling period, this variation could be explained as a result of sulfur isotopic fractionation during the oxidation process. Furthermore, we observed a negative correlation (slope =  $-6.2$  and  $r = 0.6$ , Figure 3A,B) between SOR and the  $\delta^{34}\text{S}$  value of sulfates in our samples, indicating that as oxidation of  $\text{SO}_2$  progressed, the  $\delta^{34}\text{S}$  values of sulfates decreased, making them approach  $\delta^{34}\text{S}_{\text{emission}}$  (by isotope mass balance). This negative correlation supported our hypothesis that the elevated and variable  $\delta^{34}\text{S}_{\text{sulfate}}$  values should be attributed to the isotopic fractionation during  $\text{SO}_2$  oxidation processes.

The discrepancies between  $\delta^{34}\text{S}_{\text{sulfate}}$  and  $\delta^{34}\text{S}_{\text{emission}}$  (therefore,  $\delta^{34}\text{S}_{\text{SO}_2}$ ) values have been observed, especially at low SOR levels. Forrest and Newman<sup>59</sup> measured  $\delta^{34}\text{S}$  values of  $\text{SO}_2(\text{g})$  and sulfate particles in a polluted environment with a very low SOR (average SOR = 9.9% among the three experiments), and the  $\delta^{34}\text{S}_{\text{sulfate}}$  values were  $\sim 1.5\text{--}2.5\text{‰}$  higher than the  $\delta^{34}\text{S}_{\text{SO}_2}$  values. Saltzman<sup>41</sup> conducted a similar experiment at Hubbard Brook Experimental Forest, New Hampshire, and observed a  $\sim 3\text{‰}$  difference between  $\delta^{34}\text{S}_{\text{sulfate}}$  and  $\delta^{34}\text{S}_{\text{SO}_2}$  values when the SOR was  $<40\%$ . Later studies by Guo et al.<sup>38</sup> and Chen et al.<sup>39</sup> have suggested that the  $\delta^{34}\text{S}_{\text{sulfate}} - \delta^{34}\text{S}_{\text{SO}_2}$  values at Nanjing ranged between  $\sim 1$  and  $7\text{‰}$  during fall 2014 and winter 2015. These differences have suggested that the  $\delta^{34}\text{S}_{\text{sulfate}}$  values may deviate from the  $\delta^{34}\text{S}_{\text{emission}}$  values by several permil, especially when the SOR value was low. This deviation might complicate the use of  $\delta^{34}\text{S}_{\text{sulfate}}$  to calculate the sources of  $\text{SO}_2$  in urban regions, since most urban (anthropogenic)  $\text{SO}_2$  sources have a narrow range of  $\delta^{34}\text{S}$  values<sup>45,57</sup> ( $+1$  to  $+11\text{‰}$ ), which could be potentially altered by the isotopic fractionations during the formation of the sulfate when the SOR was low. This uncertainty might be reduced by analyzing other minor sulfur isotopes ( $^{33}\text{S}$ ,  $^{35}\text{S}$ , and  $^{36}\text{S}$ )<sup>47–51</sup> but this is beyond the scope of our work. Therefore, extra caution must be taken when using  $\delta^{34}\text{S}$  values to estimate the sources of  $\text{SO}_2$  in the urban environment with the low SOR.

The observed differences in  $\delta^{34}\text{S}_{\text{sulfate}}$  and  $\delta^{34}\text{S}_{\text{emission}}$  values can be explained using the Rayleigh distillation model, and the isotopic enrichment factor ( $\epsilon = (\alpha - 1) \times 1000\text{‰}$ ) for the total oxidation processes can also be quantified. The Rayleigh distillation model<sup>42,60</sup> is used to calculate the kinetic isotopic fractionation of a reaction ( $\text{A} \rightarrow \text{B}$ ) in an open system by assuming no isotopic exchange between A and B. In aqueous solution,  $\text{SO}_2(\text{g})$  dissolving into aerosol water was 2–3 orders of magnitude faster than the subsequent oxidation into  $\text{SO}_4^{2-}$ ; thus, the isotopic fractionation should be controlled by the kinetic isotopic effect occurring during any aqueous  $\text{SO}_2$  oxidation process.<sup>35</sup> In this model, the  $\delta^{34}\text{S}$  value of  $\text{SO}_2$  is a function of  $\delta^{34}\text{S}_{\text{emission}}$ , the fraction ( $f$ ) of remaining  $\text{SO}_2$  ( $f = 1 - \text{SOR}$ ), and the observed fractionation factor of the oxidation process ( $\epsilon_{\text{obs}}$ )

$$\delta^{34}\text{S}_{\text{SO}_2} = \delta^{34}\text{S}_{\text{emission}} + \ln(f) \times \epsilon_{\text{obs}} \quad (1)$$

Thus  $\delta^{34}\text{S}_{\text{sulfate}}$  is

$$\delta^{34}\text{S}_{\text{sulfate}} = \delta^{34}\text{S}_{\text{emission}} - \epsilon_{\text{obs}} \times \ln(f) \times f / (1 - f) \quad (2)$$

Using the observed  $\delta^{34}\text{S}_{\text{sulfate}}$ ,  $f$ , and the estimated  $\delta^{34}\text{S}_{\text{emission}}$  during our sampling period ( $2.7 \pm 1.0\text{‰}$ ), we found that the  $\epsilon_{\text{obs}}$  values ranged from 2.2 to  $10.0\text{‰}$  (Figure 3B) with an average value of  $+5.3 \pm 1.8\text{‰}$  ( $1\sigma$ ).

This changing  $\epsilon_{\text{obs}}$  value suggests that multiple  $\text{SO}_2$  oxidation pathways have contributed to the observed sulfate accumulation. At 273 K (average temperature during the sampling period), OH oxidation enriches  $^{34}\text{S}$  in the product sulfate with an enrichment factor ( $\epsilon_{\text{OH}}$ ) of  $+11.0\text{‰}$ ,<sup>35</sup> and oxidation by the TMI pathway depletes  $^{34}\text{S}$  ( $\epsilon_{\text{TMI}} = -5.0\text{‰}$ ) in the product sulfate with a  $\epsilon_{\text{TMI}}$  value of  $-5.0\text{‰}$ .<sup>35,36</sup> Several laboratory experiments<sup>35–37</sup> measured the  $\epsilon$  values of  $\text{SO}_2 + \text{O}_3$  and  $\text{SO}_2 + \text{H}_2\text{O}_2$ , and these two pathways showed similar  $\epsilon$  values ranging from  $+15.1$  to  $+17.4\text{‰}$ . Therefore, here we use  $\epsilon_{\text{O}_3/\text{H}_2\text{O}_2} = +15.1\text{‰}$  to represent the combined isotopic effect of  $\text{O}_3$  and/or  $\text{H}_2\text{O}_2$  pathways. Since the variation of temperature during the entire sampling period was small (the standard deviation of  $\pm 3.7$  K), the variations of the fractionation factors ( $<1\text{‰}$ ) were insignificant comparing to the differences

between the fractionation factors ( $\sim 20\%$ ). Therefore, in the following calculation, we assume that the fractionation factors are constants. The  $\epsilon_{\text{obs}}$  value does not agree with any of the laboratory-determined  $\epsilon$  values, suggesting that none of the pathways had a dominant role in the formation of the sulfate. Instead, the  $\epsilon_{\text{obs}}$  should be a result of the mixing of multiple oxidation pathways

$$\epsilon_{\text{obs}} = \epsilon_{\text{O}_3/\text{H}_2\text{O}_2} \times f_{\text{O}_3/\text{H}_2\text{O}_2} + \epsilon_{\text{TMI}} \times f_{\text{TMI}} + \epsilon_{\text{OH}} \times f_{\text{OH}} \quad (3)$$

in which  $\epsilon_i$  and  $f_i$  are the enrichment factor and the contribution of the pathway  $i$ , and  $f_{\text{O}_3/\text{H}_2\text{O}_2} + f_{\text{TMI}} + f_{\text{OH}} = 1$ .

The sulfate formed via the gas-phase  $\text{SO}_2 + \text{OH}$  pathway was calculated to be unimportant. Concentrations of the OH radical were first obtained using a zero-dimensional (0-D) atmospheric chemistry model coupled with time-dependent photochemistry. The model used the tropospheric ultraviolet and visible (TUV) radiation model<sup>61</sup> to determine the molecular photolysis frequencies ( $j$  values) for the major molecules ( $\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{NO}_3$ , HONO,  $\text{N}_2\text{O}_5$ ,  $\text{H}_2\text{O}_2$ , and other organic molecules) during the sampling period for a time step of 3 h. Subsequently calculated  $j$  values were incorporated into a 0-D atmospheric chemistry model driven by the "regional atmospheric chemistry modeling" (RACM) mechanism.<sup>62</sup> The model then calculated time-dependent OH radical concentrations using average concentrations of trace gases ( $\text{O}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$ ) during the pollution period. The OH concentrations display clear diurnal variation, with the peak concentration of  $1.35 \times 10^6$  molecules/ $\text{cm}^3$  at noon, and a daily average value of  $0.31 \times 10^6$  molecules/ $\text{cm}^3$ , similar to the observed winter OH concentrations in other urban areas.<sup>63,64</sup> The reaction rates of gas-phase  $\text{SO}_2$  oxidation ( $\text{SO}_2 + \text{OH}$ ) were then calculated using

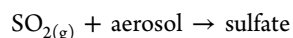
$$d[\text{SO}_4^{2-}]/dt = k \times [\text{SO}_2] \times [\text{OH}] \quad (4)$$

in which  $k$  is the reaction constant<sup>5</sup> at 273 K ( $1.5 \times 10^{-12}$  molecules $^{-1} \times \text{cm}^3 \times \text{s}^{-1}$ ),  $[\text{SO}_2]$  and  $[\text{OH}]$  are observed  $\text{SO}_2$  concentrations and calculated OH concentrations. The results (the gray line in Figure 2B) suggest that the OH oxidation rate averaged at  $0.05 \mu\text{g}/\text{m}^3/\text{h}$  during the entire sampling period, and the maximum oxidation rate with the highest OH concentration at noon was only  $0.3 \mu\text{g}/\text{m}^3/\text{h}$ . Since the measured sulfate accumulation rates were 1.3 and  $2.1 \mu\text{g}/\text{m}^3/\text{h}$  during the two accumulation events, and assuming a negligible sulfate dry deposition of  $0.1 \text{ cm}/\text{s}$ <sup>65</sup> and an average boundary layer height of 600 m, the sulfate production rates during the two events were 1.55 and  $2.38 \mu\text{g}/\text{m}^3/\text{h}$ . These estimated sulfate production rates were 26–46 times faster than the average OH oxidation rate. A similar low sulfate production via gas-phase oxidation was also inferred during winter haze episodes in Beijing.<sup>17</sup> This low contribution (2–3%) of gas-phase sulfate production was probably because of a combination of weak photochemistry in winter, a high aerosol concentration that scattered light, and extremely high heterogeneous and aqueous oxidations in haze episodes.<sup>11,66,67</sup> Therefore,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , and TMI pathways should be the dominant contributors to the observed high sulfate production, and eq 3 can be simplified as

$$\epsilon_{\text{obs}} = \epsilon_{\text{O}_3/\text{H}_2\text{O}_2} \times f_{\text{O}_3/\text{H}_2\text{O}_2} + \epsilon_{\text{TMI}} \times f_{\text{TMI}} \quad (5)$$

Equation 5 can be used to estimate the role of heterogeneous and aqueous oxidations of  $\text{SO}_{2(\text{g})}$  by  $\text{O}_3$ ,

$\text{H}_2\text{O}_2$ , and TMI-catalyzed  $\text{O}_2$  that were likely to be responsible for the fast accumulation of sulfate aerosols during the haze episode. This hypothesis is further confirmed by applying a pseudo-first-order uptake process to estimate heterogeneous and aqueous sulfate production.<sup>1</sup> This approach treats  $\text{SO}_2$  oxidation on/in the aerosols as a first-order uptake reaction on the surface of the aerosols:



Its rate is expressed as<sup>1,17,68</sup>

$$d[\text{SO}_4^{2-}]/dt_{\text{het}} = (R_a/D_g + 4/\gamma\nu)^{-1} \times S_a \times [\text{SO}_2] \quad (6)$$

in which  $D_g$  ( $2 \times 10^{-5}$ ) is the  $\text{SO}_2$  diffusion coefficient,<sup>68</sup>  $\nu$  ( $300 \text{ m}^2/\text{s}$ ) is the  $\text{SO}_2$  mean molecular velocity,<sup>68</sup> and  $R_a$  is the effective radius of aerosols, which is estimated using the following equation that was empirically derived from two haze episodes in Beijing<sup>2</sup>

$$R_a = (0.254 \times [\text{PM}_{2.5}]/(\mu\text{g}/\text{m}^3) + 10.259) \times 10^{-9} \text{ m} \quad (7)$$

$S_a$  is the aerosol surface area density ( $\text{cm}^2/\text{cm}^3$ ) estimated using the average aerosol effective radius and the average density ( $\rho$ ) of  $\text{PM}_{2.5}$  ( $1.5 \text{ g}/\text{cm}^3$ )

$$S_a = [\text{PM}_{2.5}] \times 3/(R_a \times \rho) \quad (8)$$

and  $\gamma$  is the  $\text{SO}_2$  uptake coefficient. Although laboratory-determined  $\gamma$  values of  $\text{SO}_2$  uptake can vary by several orders of magnitude depending on the surface property, particle compositions, temperature, and RH, previous modeling works have shown that setting the average  $\gamma$  values as a function of relative humidity<sup>1</sup> would best match the modeled sulfate to observations

$$\gamma = \max(2.0 \times 10^{-5}, 6.0 \times 10^{-7} \times \text{RH}(\%) - 1 \times 10^{-5}) \quad (9)$$

The calculated sulfate production rates ranged from 0.8 to  $5.2 \mu\text{g}/\text{m}^3/\text{h}$  with a mean value of  $2.3 \mu\text{g}/\text{m}^3/\text{h}$  during the sampling period (Figure 2B), similar to the observed sulfate accumulation rates ( $1.5$  and  $2.1 \mu\text{g}/\text{m}^3/\text{h}$ ). Therefore, this calculation implies that heterogeneous and aqueous oxidations via  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , and TMI pathways were the main sources of sulfates during the haze episode. The overall calculated sulfate production rate agrees well with the observed data, but this approach seems to be overestimating the sulfate production during Event I by  $\sim 80\%$  ( $2.79 \mu\text{g}/\text{m}^3/\text{h}$  vs observed  $1.55 \mu\text{g}/\text{m}^3/\text{h}$ ) and underestimating the sulfate production in Event II by  $\sim 44\%$  ( $1.32 \mu\text{g}/\text{m}^3/\text{h}$  vs observed  $2.38 \mu\text{g}/\text{m}^3/\text{h}$ ). Since the  $\text{PM}_{2.5}$  mass and hence aerosol surface area were similar between the two events ( $141 \pm 41 \mu\text{g}/\text{m}^3$  in Event I vs  $171 \pm 24 \mu\text{g}/\text{m}^3$  in Event II) but the RH in Event II ( $81 \pm 2\%$ ) was higher than Event I ( $57 \pm 17\%$ ), and that the  $\text{SO}_2$  uptake coefficient is a function of RH, we suggest that this discrepancy might be due to the over-/underestimation of the  $\text{SO}_2$  uptake coefficient at low/high RH. The calculated  $\text{SO}_2$  uptake coefficient ranged from  $2 \times 10^{-5}$  to  $5 \times 10^{-5}$  but experimental data has shown that these coefficients are a function of the aerosol surface material.  $\text{SO}_2$  uptake coefficients can be as low<sup>69</sup> as  $0.41 \times 10^{-5}$  on Sahara dust or as high<sup>70</sup> as  $6.6 \times 10^{-5}$  on iron oxides. Therefore, we suggest that the pseudo-first-order uptake process estimation<sup>1</sup> showed general agreement with the observed average production rate, although it is

possible to under-/overestimate the uptake coefficients (therefore the oxidation rate) over a short time period at certain conditions because of the heterogeneity of aerosol compositions.

These calculations suggest that the sulfate in the haze episode was primarily controlled by the heterogeneous and aqueous oxidations via  $O_3$ ,  $H_2O_2$ , and TMI pathways, enabling us to use the  $\epsilon_{obs}$  and eq 5 to estimate the contributions of the oxidation pathways. The overall  $\epsilon_{obs}$  value ( $+5.3 \pm 1.8\%$ ) falls in between  $\epsilon_{O_3/H_2O_2}$  and  $\epsilon_{TMI}$  values, indicating that both  $O_3/H_2O_2$  and TMI pathways played important roles in the oxidation process. Using eq 5, we determined that the overall contributions from TMI and  $O_3/H_2O_2$  pathways (Figure 3C) were roughly equal ( $f_{TMI} = 49 \pm 10\%$  and  $f_{O_3/H_2O_2} = 51 \pm 10\%$ ) during the haze episode. Notably, however, there were two time periods (at the end of  $PM_{2.5}$  accumulation events I and II) when decreases in the  $\epsilon_{obs}$  values were observed. In the first time period (January 24, 6:00–18:00), the sulfate concentration increased by  $\sim 100\%$ , the SOR remained steady, while the  $\delta^{34}S_{sulfate}$  values decreased from 8.4 to  $+4.6\%$ . The calculated  $\epsilon_{obs}$  values, thus, have decreased from 7.2 to  $2.8\%$ , suggesting that the TMI pathway has played a more important role during this process. The second time period (January 25, 12:00 to January 26, 3:00) was similar when the sulfate concentration increased by  $\sim 180\%$  and the  $\epsilon_{obs}$  value decreased from 9.9 to  $3.4\%$ . Both events were associated with high  $PM_{2.5}$  and low  $O_3$  concentrations. The decreased  $\epsilon_{obs}$  values suggested elevated contributions of the TMI pathway (accounting for 57–62% of sulfate production). The increased TMI pathway contribution likely resulted from a combination of two factors. First, the high aerosol concentrations, which likely provided a high aerosol surface area and a high amount of transition-metal ions (e.g., Fe, Mn, Cu, Zn, and Pb), from local industrial emission<sup>71</sup> could enhance the rate of TMI oxidation. Second, the  $O_3/H_2O_2$  oxidation rate was likely decreased due to decreased  $O_3$  concentrations and the liquid water content. The average  $O_3$  concentrations ( $6.2$  and  $5.0 \mu\text{g}/\text{m}^3$ ) and RH (51 and 65%) during these two periods were significantly lower than those of the rest of the haze episode (averaging  $13.0 \mu\text{g}/\text{m}^3$   $O_3$  and 81% RH), which might reduce the oxidation rate of  $O_3/H_2O_2$ . However, since it is difficult to quantitatively determine the rate of the TMI pathway and the accurate pH of aerosol water, therefore, the rate of  $O_3$  oxidation, either the factor or both factors could be the dominant cause. A future experimental work is needed to separately investigate the effects of the aerosol surface area, transition-metal ion concentrations, RH,  $O_3$  concentration, etc., on each oxidation pathway.

The significant contribution from the TMI pathway ( $49 \pm 10\%$ ) suggests an elevated role of the TMI pathway during the rapid formation of sulfate aerosols in the haze episode, showing general agreement with atmospheric chemistry modeling studies. Globally, the TMI pathway was estimated to contribute to 9–18% of total aerosol production,<sup>8,10</sup> in most regions in China (including Nanjing); model simulations suggested that TMI had played a more important role, contributing to  $\sim 20$ –50% of total sulfate production.<sup>10</sup> Harris et al.<sup>35</sup> also pointed out that at least 35% of the sulfate in several Chinese cities<sup>44</sup> was produced via the TMI pathway. During haze episodes, the contributions of the TMI pathway among the heterogeneous and aqueous oxidations seem to increase; a recently developed modeling study<sup>22</sup> suggests that

the TMI pathway was responsible for as much as 80% of total heterogeneous and aqueous sulfate production during haze episodes in Beijing, and oxygen isotopic evidence suggested similar contributions (66–73%).<sup>17</sup> Furthermore, the field observation work at another heavily polluted region (Fort McMurray, Alberta, Canada) also implied the importance of the TMI pathway during the formation of the secondary sulfate.<sup>72</sup> Our study had pointed out that the TMI pathway was an important but probably not the sole sulfate formation pathway during the haze episodes, and its contribution was likely elevated during the haze episodes. The increased contribution of the TMI pathway during haze episodes might originate from a combination of high aerosol surface, high atmospheric liquid water content, and dust flux. In the meantime, the  $O_3$  and/or  $H_2O_2$  also played a major role in the formation of sulfate aerosols despite their lower-than-typical concentrations. Therefore, to improve the simulation of sulfate aerosol formation, all of the above reactions (aqueous  $O_3$ ,  $H_2O_2$ , and TMI oxidations and heterogeneous  $O_3$ ,  $H_2O_2$ , and TMI oxidations) should be carefully parameterized in atmospheric chemistry models.

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## Notes

The authors declare no competing financial interest.

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