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Quantifying SO_2 oxidation pathways to atmospheric sulfate by using stable sulfur and oxygen isotopes: laboratory simulation and field observation

Ziyan Guo[a], Keding Lu[a]*, Pengxiang Qiu[b], Mingyi Xu[b], Zhaobing Guo[b*]

[a] State Key Joint Laboratory of Environmental Simulation and Pollution Control, State Environmental Protection Key Laboratory of Atmospheric Ozone Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, China.

[b] Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), Collaborative Innovation Center of Atmospheric Environment and Equipment Technology (CIC-AEET), School of Environmental Science and Engineering, Nanjing University of Information Science and Technology, Nanjing 210044, China

*Correspondence to: *k.lu@pku.edu.cn (Keding Lu), guocumt@nuist.edu.cn (Zhaobing Guo)*

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Abstract. The formation of secondary sulfate in the atmosphere remains controversial, and it is urgent to seek for a new method to quantify different sulfate formation pathways. Thus, SO_2 and $PM_{2.5}$ samples were collected from 4 to 22 Dec. 2019 in Nanjing. Sulfur and oxygen isotope compositions were synchronously measured to study the contribution of SO_2 homogeneous and heterogeneous oxidation to sulfate. Meanwhile, the correlation of $\delta^{18}O$ values between H_2O and sulfate from SO_2 oxidation by H_2O_2 and Fe^{3+}/O_2 were investigated in the lab. Based on isotope mass equilibrium equations, the ratios of different SO_2 oxidation pathways were calculated. The results showed that secondary sulfate constituted higher than 80 % of total sulfate in $PM_{2.5}$ during the sampling period. Laboratory simulation experiments indicated that $\delta^{18}O$ of sulfate was linearly dependent on $\delta^{18}O$ of water, and the slopes of linear curves for SO_2 oxidation by H_2O_2 and Fe^{3+}/O_2 were 0.43 and 0.65, respectively. The secondary sulfate in $PM_{2.5}$ was mainly ascribed to SO_2 homogeneous oxidation by OH radicals and heterogeneous oxidation by H_2O_2 and Fe^{3+}/O_2. SO_2 heterogeneous oxidation was generally dominant during sulfate formation, and the contribution of SO_2 heterogeneous oxidation was about 52 %. Especially, SO_2 oxidation by H_2O_2 predominated in SO_2 heterogeneous oxidation reactions with an average ratio around 55 %. This study provided an insight into precisely evaluating sulfate formation pathways by combining stable sulfur and oxygen isotopes.

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1 Introduction

Sulfate is one of the prevalent components of $PM_{2.5}$ (Brüggemann et al., 2021; Huang et al., 2014; Yang et al., 2023). Sulfate makes up approximately 25% of $PM_{2.5}$ mass in Shanghai, 23% in Guangzhou and 10-33% in Beijing (Xue et al., 2016). The rapid sulfate formation is a crucial factor determining the explosive growth of fine particles and the frequent occurrence of severe haze events in China (Lin et al., 2022; Liu et al., 2020; Meng et al., 2023; Wang et al., 2021). Sulfate plays an important role in tropospheric and lower stratospheric chemical and physical processes, which significantly affects global climate change by scattering solar radiation and acting as cloud condensation nuclei (CCN) (Gao et al., 2022; Ramanathan et al., 2001). Meanwhile, sulfate exerts a significant influence on air quality and public health (Abbatt et al., 2006).

In the past decades, numerous attempts have been made to evaluate SO_2 oxidation pathways involving in homogeneous and heterogeneous reactions. Traditionally, sulfate formation mechanisms mainly include homogeneous oxidation of SO_2 by OH radicals and heterogeneous oxidation by H_2O_2, O_3 and O_2 catalyzed by transition metal ions (TMIs) in cloud/fog water droplets. The relative importance of different sulfate formation pathways is strongly dependent on oxidant concentrations, occurrence of fog/cloud events and pH of aqueous phase (Seinfeld et al., 2016; Kuang et al., 2022; Oh et al., 2023). Generally, SO_2 homogeneous oxidation by OH and heterogeneous oxidation by H_2O_2 are considered the most important pathways for sulfate production on the global scale (Seinfeld et al., 2006). The photochemical reactivity during the winter in Beijing has been found to be relatively high, which favors the formation of reactive species such as OH radicals and H_2O_2, thereby facilitating SO_2 oxidation (Zhang et al., 2020). Xue et al. (2014) suggested that SO_2 oxidation by O_3 and H_2O_2 in aqueous phase contributed to the majority of total sulfate production. Liu et al. (2020) proposed that S(IV) oxidation by H_2O_2 in aerosol water could be an important pathway considering the ionic strength effect. He et al. (2018) found that the contribution of SO_2 oxidation by H_2O_2 could reach 88 % during Beijing haze period. Ye et al. (2018) observed that SO_2 oxidation rate by H_2O_2 was 2-5 times faster than the summed rate of the other three oxidation pathways. As a result, actual contribution of SO_2 oxidation by H_2O_2 during the winter might be underestimated in previous studies.

In addition, the presence of NO_2 was obviously favorable for SO_2 oxidation under the conditions of high RH and NH_3. NH_3 can promote the hydrolysis of NO_2 dimers to HONO and result in more sulfate

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formation on particle surface in humid conditions. However, this conclusion was doubted by Liu et al. (2017) who believed that the reaction on actual fine particles with pH at 4.2 was too slow to account for sulfate formation. Li et al. (2020) deemed that SO_2 oxidation by NO_2 might not be a major oxidation pathway in China. Furthermore, GEOS-Chem modeling study suggested that NO_2 oxidation contributed less than 2% of total sulfate production. It is found that TMI pathway was very important in highly polluted regions, and the contribution of metal-catalyzed SO_2 oxidation to sulfate was as high as 49±10% in haze. Wang et al. (2021) also argued that SO_2 oxidation by TMI on aerosol surface could be the dominant sulfate formation pathway. They found that manganese-catalyzed oxidation of SO_2 contributed 69.2±5.0% in sulfate production. Overall, the mechanisms for sulfate rapid growth remain unclear and controversial. Therefore, sulfate formation pathways via SO_2 oxidation need to be further explored, and it is urgent to develop a new method to quantify different sulfate formation processes.

Generally, sulfur isotopes allow for investigating SO_2 oxidation processes in the atmosphere because of distinctive isotope fractionation associated with different oxidation reactions (Harris et al., 2013). Harris et al. (2012) presented sulfur isotope fractionation factors of SO_2 oxidation by OH, O_3/H_2O_2 and iron catalysis were 1.0087, 1.0167 and 0.9905, respectively. Besides, the observed sulfur isotope fractionation of SO_2 oxidation by H_2O_2 and O_3 appeared to be no significant difference. Therefore, the results were particularly useful to determine the importance of transition metal-catalyzed oxidation pathway compared to other oxidation pathways. However, other main oxidation pathways of SO_2 could not be distinguished only based on stable sulfur isotope determination.

Oxygen isotope ratio ($\delta^{18}O$) can be used to deduce sulfate formation processes due to those different SO2 oxidation pathways affect oxygen isotope of product sulfate differently. Especially, mass-independent fractionation signals (nonzero $\Delta^{17}O$, where $\Delta^{17}O=\delta^{18}O-0.52\times\delta^{17}O$) of oxygen isotopes in sulfate are usually adopted to investigate the contributions of different SO_2 oxidation pathways. This method can identify the contribution of SO_2+O_3 pathway when high $\Delta^{17}O$ (>3‰) is measured in sulfate. However, there is presence of obvious uncertainty when interpreting the sulfate with low $\Delta^{17}O$ value (<1‰). Unfortunately, most sulfate samples in the atmosphere show $\Delta^{17}O$<1‰, suggesting a limited contribution of SO_2+O_3 pathway during sulfate formation. It is noteworthy that the contribution of $SO_2+H_2O_2$ pathway and TMI pathway is unclear if solely using $\Delta^{17}O$ (Li et al., 2020). Holt et al. (1982) found oxygen isotope was a valuable and complementary method to determine

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probable mechanisms of SO_2 oxidation to sulfate in the atmosphere. This provides us an insight into precisely evaluating sulfate formation pathways by combining oxygen and sulfur isotopes.

In this contribution, $PM_{2.5}$ samples were collected from 4 to 22 Dec. 2019 in Nanjing region. Sulfur and oxygen isotope compositions in sulfate were measured to study the contribution of SO_2 homogeneous and heterogeneous oxidation during sulfate formation. In addition, the linear relationships of $\delta^{18}O$ values between H_2O and sulfate from SO_2 oxidation by H_2O_2 and Fe^{3+}/O_2 were synchronously investigated in the lab. Based on sulfur and oxygen isotope mass equilibrium equations, the ratios of different SO_2 oxidation pathways during the sampling period were calculated. The study aims to seek for a novel method to quantify different SO_2 oxidation processes with sulfur and oxygen isotopes.

2 Materials and methods

2.1 Sampling location

$PM_{2.5}$ and SO_2 in the atmosphere were sampled from 4 to 22 Dec. 2019 in Nanjing, China. The sampling site was located at the roof of the library in Nanjing University of Information Science & Technology (NUIST, 32.1 ° N, 118.5 ° E), which is depicted in Fig. 1. The sampling location is at the side of Ningliu Road and closely next to Nanjing chemical industry park. There is presence of some large-scale chemical enterprises such as Nanjing steel plant, Nanjing thermal power plants and Nanjing petrochemical company, which inevitably release lots of SO_2 and iron metal into the atmosphere.

2.2 $PM_{2.5}$ and SO_2 Samples collection

$PM_{2.5}$ and SO_2 were sampled using a modified JCH-1000 sampler (Juchuang Co., Qingdao) with a flow rate of 1.05 $m^3 min^{-1}$ from 8 am to 8 pm from 4 to 22 Dec. 2019. $PM_{2.5}$ and SO_2 were collected with quartz filter (203×254 mm, Munktell, Sweden) and glass fiber filter (203×254 mm, Tisch Environment INC, USA), respectively. The filters were incinerated in a muffle furnace at 450 ℃ for 2h and then preserved in the desiccators at room temperature. The glass fiber filters were firstly soaked in 2% K_2CO_3 and 2% glycerol solution for 2h and dried in DGG-9070A electric oven. SO_2 can be changed into sulfite immediately during the sampling.

2.3 Extractions of water-soluble sulfate

$PM_{2.5}$ sample filters were shredded and soaked in 400 mL of Milli-Q (18 MΩ) water for extractions

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of water-soluble sulfate. Filters were then isolated from solutions by centrifugation and water-soluble sulfate was precipitated as $BaSO_4$ by adding 1 mol L^{-1} $BaCl_2$. After the filtration with 0.22 μm acetate membrane, $BaSO_4$ precipitate was rinsed with Milli-Q water to remove Cl^-. Finally, $BaSO_4$ powers were calcined at 800 ℃ for 2h to obtain high purity $BaSO_4$. In addition, a small amount of H_2O_2 solution was added to oxidize sulfite to sulfate.

2.4 Laboratory simulation of SO_2 oxidation by H_2O_2 and Fe^{3+}/O_2

For SO_2 oxidation by H_2O_2, 30 mL min^{-1} Ar was firstly introduced into three kinds of different water about 30 min to drive out air. Sulfate was produced by adding 10 mL H_2O_2 dilute solution (0.1 mL 30% H_2O_2 in 50 mL water) to SO_2 in the reaction chamber at 10 ℃. H_2O_2 solution was agitated vigorously for 1min before admission of air. For Fe^{3+} catalyzed oxidation of SO_2, 2 mL min^{-1} SO_2 and 2 mL min^{-1} O_2 were simultaneously put into Fe^{3+} dilute solution at 10 ℃. Then, 10 mL 1 mL min^{-1} $BaCl_2$ was added to prepare $BaSO_4$. Oxygen isotope compositions of product sulfate and three kinds of water were measured to study their linear relationships.

2.5 Sulfur and oxygen isotope determination

Sulfur isotope compositions in sulfate were analyzed using Elemental analyzer (EA, Flash 2000, Thermo) and isotope mass spectrometer (IRMS, Delta V Plus, Finningan). High-purity $BaSO_4$ was converted into SO_2 in EA in the presence of Cu_2O. SO_2 from EA was ionized and $\delta^{34}S$ value was measured using IRMS. For the determination of $\delta^{18}O$, $BaSO_4$ pyrolysis was conducted in graphite furnace at 1450 ℃, and $\delta^{18}O$ value was obtained in CO produced from the pyrolysis at continuous-flow mode. The results of $\delta^{34}S$ and $\delta^{18}O$ were with respect to international standard V-CDT and V-SMOW, and the accuracy were better than ±0.2‰ and ±0.3‰, respectively.

3 Results and discussion

3.1 Concentrations of $PM_{2.5}$, sulfate and SO_2

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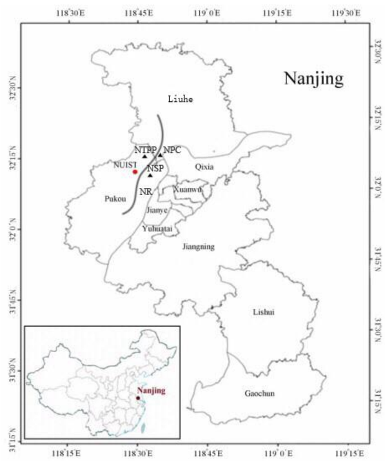

Fig.1. Sampling site of NUIST in Nanjing, China. NSP: Nanjing steel plants; NTPP: Nanjing thermal power plants; NPC: Nanjing petrochemical company; NR: Ningliu Road.

As described in Fig. 2, the mass concentrations of $PM_{2.5}$, SO_4^{2-} and SO_2 during the period from 4 to 22 Dec. 2019 in NUIST changed from 28.1 to 67.0 μg m^{-3}, 8.3 to 17.8 μg m^{-3} and 6.2 to 20.9 μg m^{-3} with an average and standard deviation at 45.7±12.1 μg m^{-3}, 12.7±3.3 μg m^{-3} and 10.2±4.4 μg m^{-3}, respectively. It can be observed that $PM_{2.5}$ average concentration was about 1.3 times of the First Grade National Ambient Air Quality Standard (35 μg m^{-3}) and beyond the safety standard of World Health Organization (10 μg m^{-3}). The photochemical reactivity during the winter in Beijing has been found to be relatively high (Zhang et al., 2020), which facilitates the formation of some photooxidants. The relatively clean days during the sampling period indicates the importance of photoinduced oxidation of SO_2.

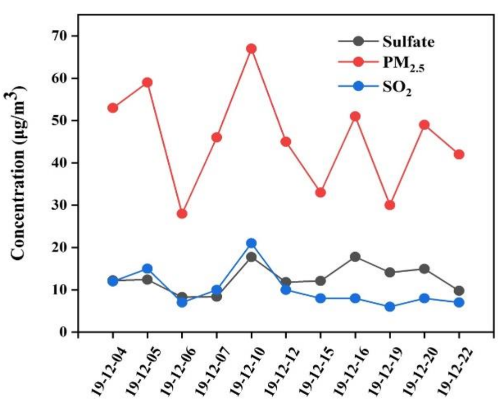

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Fig. 2. The concentrations of $PM_{2.5}$, SO_4^{2-} and SO_2.

Meanwhile, the change trends of $PM_{2.5}$, SO_4^{2-} and SO_2 concentrations were found to be basically the same during the sampling period, suggesting sulfate was mainly from SO_2 oxidation. Especially, $PM_{2.5}$, SO_4^{2-} and SO_2 concentrations increased to the maximum values on 10 Dec.. It is noted that NO_2 and CO concentrations were 85 and 1.60 μg m^{-3} on 10 Dec., which were also the maximum values during the sampling period. High CO concentration indicates that the pollution was mainly from local emissions. However, O_3 concentration on 10 Dec. was the minimum value at 24 μg m^{-3}, which preliminarily indicates that SO_2 oxidation by NO_2 might be a major pathway in sulfate formation. Previous studies showed that SO_2 oxidation by NO_2 in aerosol water dominated heterogeneous sulfate formation during wintertime at neutral aerosol pH (Wang et al., 2016; Cheng et al., 2016). However, subsequent studies showed that the calculated aerosol pH was in the range of 4.2～4.7, and the reactions between SO_2 and NO_2 during this pH range were too slow to produce sulfate. Taking into account low aerosol pH in Nanjing region, we suggested that SO_2 oxidation by NO_2 was not a dominant pathway for sulfate formation during the sampling period.

In contrast, $PM_{2.5}$, SO_4^{2-} and SO_2 concentrations were observed to be at the minimum values On 6 Dec.. Similarly, NO_2 and CO concentrations were also at the minimum of 36 and 0.6 mg m^{-3}, respectively. However, O_3 concentration on 6 Dec. was the maximum at 50 μg m^{-3}. Besides, the rate of SO_2 oxidation with O_3 becomes fast only when pH>5, the reaction rate of SO_2 with O_3 is one hundredth of those with H_2O_2 or TMI when pH<5. Therefore, pH values of actual fine particles at 4～5 in Nanjing could markedly restrain SO_2 oxidation by O_3. The lowest SO_4^{2-} concentration on 6 Dec. further demonstrated that SO_2 oxidation by O_3 played an insignificant role in sulfate formation.

Generally, aqueous-phase oxidation is deemed to be a main process of sulfate formation in atmospheric environment. Shao et al. (2018) believed that heterogeneous sulfate production on aerosols occurred when relative humidity (RH) was higher than 50 %. The RH values of the atmosphere ranging from 50.7 to 88.9% during the sampling period indicated that sulfate formation was closely related to the heterogeneous oxidation of SO_2.

3.2 Sulfur isotope compositions in sulfate and SO_2

It can be observed from Fig. 3 that the values of $\delta^{34}S\text{-}SO_4^{2-}$ were generally higher compared to those of $\delta^{34}S\text{-}SO_2$ during the sampling period except that on 16 Dec.. The $\delta^{34}S\text{-}SO_4^{2-}$ values ranged from 3.1

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to 4.7‰ with an average and standard deviation at 4.0±0.6‰, while $\delta^{34}S$-SO_2 values changed from -2.9 to 4.7‰ with an average and standard deviation at -0.2±2.3‰. The discrepancy between the values of $\delta^{34}S$-SO_4^{2-} and $\delta^{34}S$-SO_2 was mainly related to sulfur isotope fractionation effect during SO_2 oxidation to secondary sulfate.

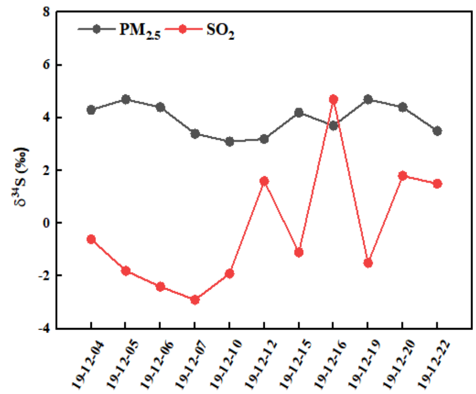

Fig. 3. Sulfur isotope compositions in sulfate and SO_2.

It is noteworthy that the values of $\delta^{34}S$-SO_4^{2-} were similar to that in $PM_{2.5}$ with an average at 4.2‰ during Youth Olympic Games in Aug. 2014 in Nanjing (Guo et al., 2016). However, the average value of $\delta^{34}S$-SO_4^{2-} during the sampling period was lower than 5.6‰ in Nanjing during a typical haze event from 21 Dec. 2015 to 1 Jan. 2016 (Guo et al., 2019). The higher $\delta^{34}S$ values of sulfate in haze was possibly ascribed to SO_2 heterogeneous oxidation, which typically enriched heavy sulfur isotope in sulfate. In this study, the average concentrations of $PM_{2.5}$ was 45.7 μg m^{-3}, indicating a not heavily polluted time interval. Besides, the relatively high temperature during the sampling period was favorable for photochemical reactions and OH radicals formation. As a result, the contribution of SO_2 homogenous oxidation increased during sulfate formation, which enriched light sulfur isotope compared to that in haze. Han et al. (2017) determined $\delta^{34}S$ values in Beijing $PM_{2.5}$ with an average at 6.0‰. It is observed that there existed a regional difference in $\delta^{34}S$-SO_4^{2-} values. The $\delta^{34}S$-SO_4^{2-} in Nanjing was generally lower than that in Beijing. The discrepancy of $\delta^{34}S$-SO_4^{2-} illustrated different sulfur sources and SO_2 oxidation pathways in these regions. In addition, $\delta^{34}S$-SO_4^{2-} values presented a seasonal change. $\delta^{34}S$ values in Beijing aerosol sulfate varied from 3.4 to 7.0‰ with an average of 5.0‰ in summer and from 7.1 to 11.3‰ with an average of 8.6‰ in winter. Generally, the homogeneous oxidation of SO_2 dominated in summer compared to that in winter due to strong solar

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irradiation (Han et al., 2016). SO_2 oxidation might lead to sulfur isotope fractionation, which was mainly attributed to equilibrium or kinetic discrimination between SO_2 and sulfate. The influence of different oxidants on sulfur isotope fractionation needed to be further investigated.

Fig.4 presents the relationship between $\delta^{34}S\text{-}SO_4^{2-}$ and atmospheric temperature during the sampling period. It can be observed that there existed an obviously negative correlation. The higher temperature generally corresponded to the lower $\delta^{34}S\text{-}SO_4^{2-}$. This is mainly ascribed to kinetic effect of sulfur isotope fractionation during SO_2 oxidation. At high temperature, more OH radicals were produced and the contribution of SO_2 homogeneous oxidation increased. It is reported that sulfur isotope fractionation about SO_2 was -9‰ for homogeneous oxidation process (Tanaka et al., 1994). Therefore, low $\delta^{34}S$ value in sulfate at high temperature was chiefly due to elevated SO_2 homogeneous oxidation.

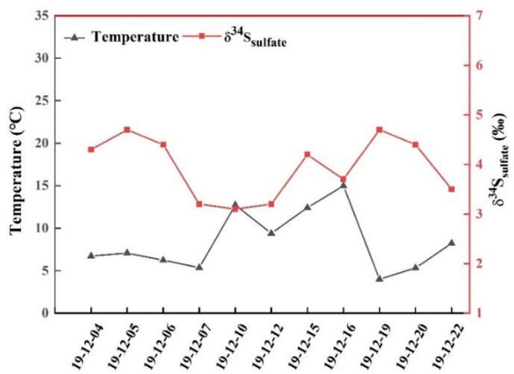

Fig. 4. The relationship between $\delta^{34}S\text{-}SO_4^{2-}$ and atmospheric temperature.

3.3 Sulfur isotope fractionation during SO_2 oxidation

The secondary sulfate was generally from SO_2 homogeneous and heterogeneous oxidation (Seinfeld et al., 2016). The homogeneous and heterogeneous oxidation of SO_2 led to sulfur isotope fractionation, which is described by using fractionation coefficient (α)

$$\alpha=\frac{\frac{\delta^{34}S_{SO_4^{2-}}}{10^3}+1}{\frac{\delta^{34}S_{SO_2}}{10^3}+1} \quad (1)$$

Sulfate enriched heavy sulfur isotope (α>1) during SO_2 heterogeneous oxidation due to the presence of isotope equilibrium fractionation and kinetic fractionation. However, sulfate enriched light sulfur

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isotope (α<1) during SO_2 homogeneous oxidation for this process was only related to kinetic fractionation. As described in Fig. 5, α values ranged from 0.9988 to 1.0201, indicating there existed SO_2 homogeneous and heterogeneous oxidation during the sampling period. α value was at the minimum of 0.9988 on 16 Dec., which showed SO_2 homogeneous oxidation played a crucial role.

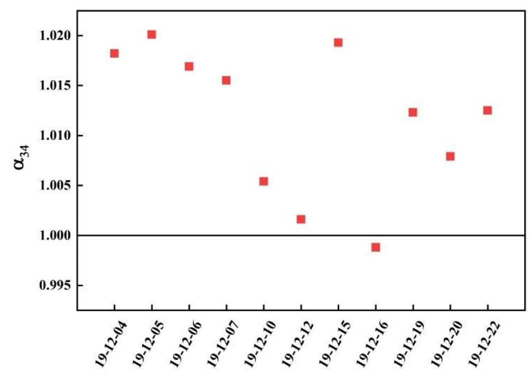

Fig. 5. Sulfur isotope fractionation coefficients during SO_2 oxidation.

It is reported that sulfur isotope fractionations during SO_2 heterogeneous and homogeneous oxidation to sulfate were 16.5‰ and -9‰, respectively (Tanaka et al., 1994). Consequently, the contribution of SO_2 heterogeneous and homogeneous oxidation to sulfate could be calculated by sulfur isotope mass equilibrium equations (2) and (3).

$$\delta^{34}S_{SO_2}+16.5x-9y=\delta^{34}S_{SO_4^{2-}} \quad (2)$$

$$x+y=1 \quad (3)$$

where x and y represent the contribution of SO_2 heterogeneous and homogeneous oxidation, respectively.

It is observed from Fig. 6 that the contribution of SO_2 heterogeneous oxidation markedly fluctuated ranging from 31.4 to 62.0% with an average and standard deviation at 51.6±0.1%, which indicated that SO_2 heterogeneous oxidation was generally dominant during sulfate formation. He et al. (2018) presented the observations of oxygen-17 excess of $PM_{2.5}$ sulfate collected in Beijing haze from Oct. 2014 to Jan. 2015, and found the contribution of heterogeneous sulfate production was about 41~54% with a mean of 48±5%. The contribution of SO_2 heterogeneous oxidation reached high-level during 5-7 Dec. and on 19 Dec., which was closely related to the temperature of the atmosphere. The low temperature about 5 ℃ in these days was favorable for SO_2 dissolution in water and further oxidized to

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sulfate by the oxidants. On 16 Dec., the contribution of SO_2 heterogeneous oxidation was the minimum at 31.4%. The highest temperature of 15 °C on 16 Dec. restrained SO_2 solubility in aqueous solution and produced lots of gaseous oxidants such as OH to promote SO_2 homogeneous oxidation.

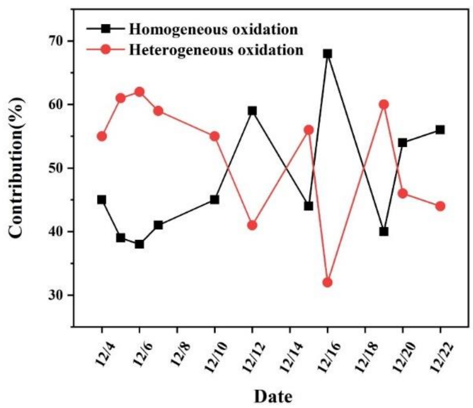

Fig. 6. The contributions of SO_2 heterogeneous and homogeneous oxidation to sulfate.

Overall, the temperature was an important factor in controlling SO_2 oxidation pathways. High temperature facilitated kinetic fractionation of sulfur isotope during SO_2 oxidation to sulfate, thereby decreasing $\delta^{34}S$ value in sulfate. In addition, it was not found to be positive correlation between the contribution of SO_2 heterogeneous oxidation and O_3 or NO_2 concentration. This also further demonstrated that SO_2 oxidation by O_3 and NO_2 were not main pathways during the sampling period. Consequently, we mainly focused on SO_2 heterogeneous oxidation by H_2O_2 and Fe^{3+}/O_2 in the following study.

3.4 The correlation of $\delta^{18}O$ between H_2O and SO_4^{2-} from SO_2 oxidation by H_2O_2 and Fe^{3+}/O_2

It is known that SO_2 rapidly equilibrates with ambient water for very high molar ratio of H_2O to SO_2 in the atmosphere. As a result, $\delta^{18}O$ of SO_2 is dynamically controlled by $\delta^{18}O$ of water and $\delta^{18}O$ of SO_2 has no obvious effect on $\delta^{18}O$ of sulfate formed by different oxidation pathways. Meanwhile, sulfate is very stable with respect to O atom exchange with ambient water. Consequently, $\delta^{18}O$ can be adopted to distinguish SO_2 oxidation processes due to that $\delta^{18}O$ of product sulfate reflected the distinctive signals of different oxidants.

In this manuscript, we firstly studied SO_2 heterogeneous oxidation by H_2O_2 and Fe^{3+}/O_2 in the lab, which aims to make clear the relationship of $\delta^{18}O$ between product sulfate and water at 10 °C. It can be

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observed from Fig. 7 that $\delta^{18}O$ of sulfate was linearly dependent on $\delta^{18}O$ of water, and the slope of linear curve for H_2O_2 oxidation approximates a ratio of 0.43, indicating that the isotopy of about two of four oxygen atoms in sulfate was controlled by $\delta^{18}O$ of water. The other two oxygen atoms were from H_2O_2 molecules, whose O-O bonds remained intact during SO_2 oxidation. In addition, we noted from Fig. 7 that the slope of linear curve for Fe^{3+}/O_2 oxidation was 0.65, which represented that the isotopy of about three of four oxygen atoms in sulfate was related to $\delta^{18}O$ of water. A 3/4 control of sulfate oxygens by water is also characteristic of heterogeneous oxidation mechanisms in which HSO_3^- isotopically equilibrated with water prior to significant oxidation to SO_4^{2-}. The other one oxygen atom in sulfate was from O_2. The higher slope suggested a higher dependence of $\delta^{18}O$ of sulfate on $\delta^{18}O$ of water during SO_2 heterogeneous oxidation by Fe^{3+}/O_2. The difference of the slope for different SO_2 heterogeneous oxidation processes provides us a novel method to distinguish SO_2 oxidation pathways.

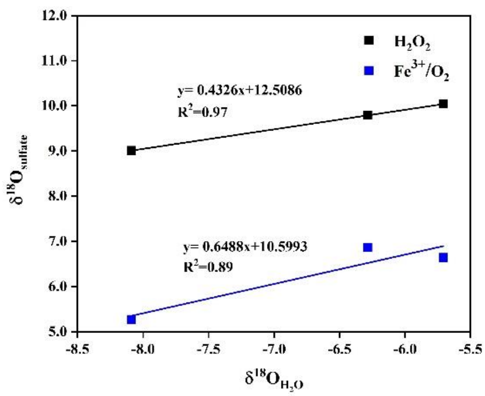

Fig.7. The correlation of $\delta^{18}O$ between H_2O and SO_4^{2-} from SO_2 oxidation by H_2O_2 and Fe^{3+}/O_2, respectively.

3.5 $\delta^{18}O$-SO_4^{2-} in $PM_{2.5}$ and SO_2 main oxidation pathways

As depicted in Fig. 8, $\delta^{18}O$ values of sulfate in $PM_{2.5}$ ranged from 11.09 to 12.93‰ with an average and standard deviation of 12.35±0.68‰. $\delta^{18}O$ values of sulfate focused on a narrow scope except those on 5 and 22 Dec.. It should be pointed out $\delta^{18}O$ value of secondary sulfate was a comprehensive result from different SO_2 oxidation processes. Sulfate in $PM_{2.5}$ usually consisted of primary sulfate and secondary sulfate. The $\delta^{18}O$ value of primary sulfate is about 38 ‰, which is significantly higher than those of secondary sulfates. The contribution of primary and secondary sulfate in the atmosphere can

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be calculated by oxygen isotope mass equilibrium equation (4) (Ben et al., 1982).

$$\delta^{18}O_{PM_{2.5}}=\delta^{18}O_{PS}\times(1-f_{SS})+\delta^{18}O_{SS}\times f_{SS} \quad (4)$$

where $\delta^{18}O_{PM_{2.5}}$, $\delta^{18}O_{PS}$ and $\delta^{18}O_{SS}$ mean $\delta^{18}O$ values of $PM_{2.5}$, primary sulfate and secondary sulfate, respectively; f_{SS} is the contribution of secondary sulfate in $PM_{2.5}$.

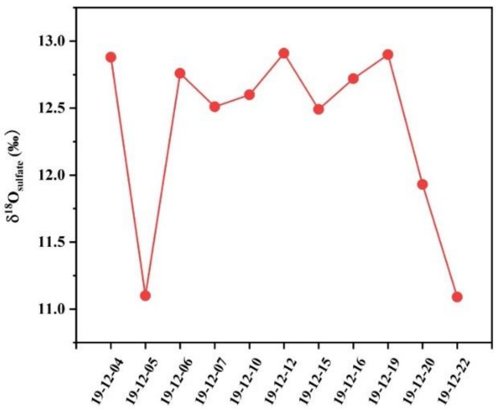

Fig.8. $\delta^{18}O$ values of sulfate in $PM_{2.5}$ during the sampling period.

Table 1 shows the contribution of primary sulfate and secondary sulfate in $PM_{2.5}$ during the sampling period. It can be observed that the majority of sulfate in $PM_{2.5}$ was secondary sulfate. Secondary sulfate appears to constitute from 80.0 to 86.1% of the total sulfate. As discussed above, secondary sulfate was mainly ascribed to SO_2 homogeneous oxidation by OH radicals and heterogeneous oxidation by H_2O_2 and Fe^{3+}/O_2. Therefore, it is admirable to quantitively describe these formation pathways of secondary sulfate in $PM_{2.5}$.

Table 1 The contribution of primary sulfate and secondary sulfate in $PM_{2.5}$.

Sampling time	Primary sulfate (%)	Secondary sulfate (%)
4 Dec.	10.9-23.7	76.3-89.1
5 Dec.	4.6-18.2	81.8-95.4
6 Dec.	10.6-23.3	76.7-89.4
7 Dec.	9.6-22.5	77.5-90.4
10 Dec.	10.0-22.8	77.2-90.0
12 Dec.	11.1-23.8	76.2-89.9
15 Dec.	9.6-22.5	77.5-90.4

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16 Dec.	11.9-23.6	76.4-88.1
19 Dec.	11.0-23.7	76.3-89.0
20 Dec.	7.7-20.8	79.2-92.3
22 Dec.	4.5-18.1	79.1-95.5

It is noteworthy that there exists a linear relationship between $\delta^{18}O$ values in water and primary sulfate or secondary sulfate from different oxidation pathways (Fig. 9), which can be described by the equations (5)-(8). $\delta^{18}O$ values of sulfate in atmospheric samples consist of those of primary sulfate and secondary sulfate. Considering the contribution of primary sulfate and secondary sulfate as well as $\delta^{18}O$ water is about -6.2‰ in Nanjing region, we can calculate the ratios of different SO_2 oxidation pathways at 10 ℃ via oxygen isotope mass equilibrium equations (9)-(11), and the corresponding results are depicted in Table 2.

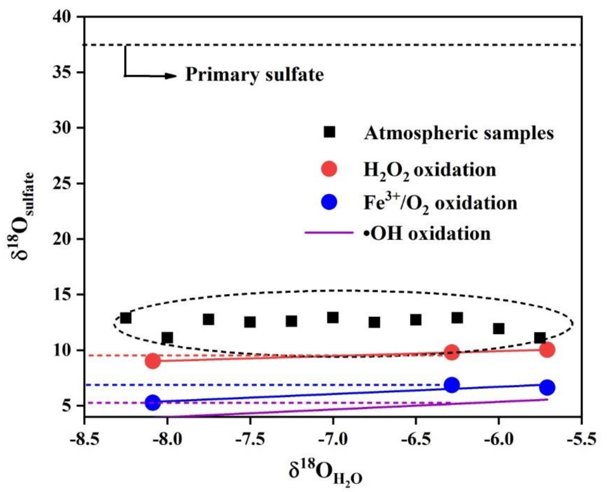

Fig.9. The correlation between $\delta^{18}O$ values in water and sulfate in $PM_{2.5}$.

$$\delta^{18}O_{sulfate}=0.06\times\delta^{18}O_{water}+38\text{ ‰}(PS)\text{ (Holt et al., 1983)} \quad (5)$$

$$\delta^{18}O_{sulfate}=0.69\times\delta^{18}O_{water}+9.5\text{ ‰ (SS, OH) (Holt et al., 1983)} \quad (6)$$

$$\delta^{18}O_{sulfate}=0.65\times\delta^{18}O_{water}+10.6\text{ ‰ (SS, }Fe^{3+}/O_2\text{) (this study)} \quad (7)$$

$$\delta^{18}O_{sulfate}=0.43\times\delta^{18}O_{water}+12.5\text{ ‰ (SS, }H_2O_2\text{) (this study)} \quad (8)$$

$$\delta^{18}O_{PM_{2.5}}=\delta^{18}O_{PS}\times f_{PS}+(\delta^{18}O_{SS\text{-}OH}\times f_{SS\text{-}OH}+\delta^{18}O_{SS\text{-}Fe^{3+}/O_2}\times f_{SS\text{-}Fe^{3+}/O_2}+\delta^{18}O_{SS\text{-}H_2O_2}\times f_{SS\text{-}H_2O_2})\times f_{SS} \quad (9)$$

$$f_{PS}+f_{SS}=1 \quad (10)$$

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$$f_{SS\text{-}OH} + f_{SS\text{-}Fe^{3+}/O_2} + f_{SS\text{-}H_2O_2} = 1 \quad (11)$$

where $\delta^{18}O_{PM_{2.5}}$ and $\delta^{18}O_{PS}$ are $\delta^{18}O$ values of total sulfate and primary sulfate in $PM_{2.5}$; $\delta^{18}O_{SS\text{-}OH}$, $\delta^{18}O_{SS\text{-}Fe^{3+}/O_2}$ and $\delta^{18}O_{SS\text{-}H_2O_2}$ are $\delta^{18}O$ values of secondary sulfate from SO_2 oxidation by OH radical, Fe^{3+}/O_2 and H_2O_2, respectively; f_{PS} and f_{SS} are the contribution of primary and secondary sulfate; $f_{SS\text{-}OH}$, $f_{SS\text{-}Fe^{3+}/O_2}$ and $f_{SS\text{-}H_2O_2}$ are the contribution of secondary sulfate from SO_2 oxidation by OH radicals, Fe^{3+}/O_2 and H_2O_2, respectively.

Unlike heavily polluted days with reduced solar irradiation, the photochemical reactivity could remain high in relatively clean days during the observation period because of intense solar irradiation. As a result, some photochemical reactive species such as OH radicals and H_2O_2 are deemed to be the major oxidants for sulfate formation. It is observed from Table 2 that the ratio of SO_2 oxidation by OH radicals ranged from 38 to 68% with an average and standard deviation at 48±9.7%. The ratio reached the maximum of 68% on 16 Dec., which is mainly ascribed to the highest temperature of 15 ℃ during the sampling period. The photochemical reactions are favorable for producing more OH radicals. In contrast, the ratio of SO_2 oxidation by OH radicals decreased to the minimum on 6 Dec. due to the low temperature.

Table 2 The ratio of SO_2 different oxidation pathways to sulfate.

Sampling time	OH oxidation ratio	H_2O_2 oxidation ratio	Fe^{3+}/O_2 oxidation ratio	Percentage of H_2O_2 oxidation in SO_2 heterogeneous reactions (%)
4 Dec.	0.45	0.27	0.28	49
5 Dec.	0.39	0.24	0.37	40
6 Dec.	0.38	0.24	0.38	39
7 Dec.	0.41	0.25	0.34	43
10 Dec.	0.45	0.27	0.28	49
12 Dec.	0.59	0.30	0.11	74
15 Dec.	0.44	0.26	0.30	47
16 Dec.	0.68	0.26	0.06	80
19 Dec.	0.4	0.25	0.35	41
20 Dec.	0.54	0.31	0.15	67

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22 Dec.	0.56	0.32	0.12	72

SO_2 heterogeneous oxidation was relatively dominant during the sampling period. It is known that SO_2 oxidation by H_2O_2 and Fe^{3+}/O_2 are the most important pathways during the heterogeneous oxidation. From table 2, the percentage of sulfate from SO_2 oxidation by H_2O_2 in total secondary sulfate from SO_2 heterogeneous oxidation reactions varied from 39 to 80% with an average and standard deviation at 54.6±15.5%, indicating that H_2O_2 oxidation predominated during SO_2 heterogeneous reactions. In addition, there existed an obviously positive correlation between the ratio of SO_2 oxidation by H_2O_2 and OH radicals, which was chiefly attributed to photochemical reactions. The relatively strong solar irradiation on 16 Dec. resulted in the maximum ratio of 80% about H_2O_2 oxidation in SO_2 heterogeneous reactions. The sampling site is near to Nanjing steel plant. As companion emitters, Fe^{3+} are present in much higher concentrations than that in other areas. It is believed that SO_2 oxidation by O_2 in the presence of Fe^{3+} was important in the areas where the concentrations of SO_2 and Fe^{3+} were high. This inevitably resulted in high Fe^{3+}/O_2 oxidation ratio in SO_2 heterogeneous oxidation reactions.

4 Conclusions

There was no serious $PM_{2.5}$ pollution during the sampling period. The secondary sulfate constitutes from about 80.0 to 86.1% of total sulfate in $PM_{2.5}$. SO_2 oxidation by O_3 and NO_2 played an insignificant role in sulfate formation. The secondary sulfate was mainly ascribed to SO_2 homogeneous oxidation by OH radicals and heterogeneous oxidation by H_2O_2 and Fe^{3+}/O_2. Compared to homogeneous oxidation, SO_2 heterogeneous oxidation was generally dominant during sulfate formation. The contribution of SO_2 heterogeneous oxidation was about 52%. SO_2 oxidation by H_2O_2 predominated in SO_2 heterogeneous oxidation reactions and the average ratio of which reached 55%.

Author contribution

Ziyan Guo analyzed the data and wrote the original draft. Keding Lu designed the methodology and administrated the project. Pengxiang Qiu and Mingyi Xu performed the data collection. Zhaobing Guo reviewed and revised the paper

Competing interests

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The authors declare that they have no known competing interests or personal relationships that could have appeared to influence the work reported in this paper.

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