

Comments and Responses

Referee #2

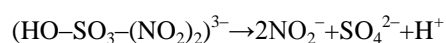
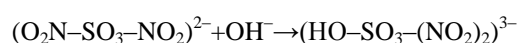
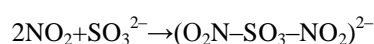
Comments: This manuscript presents a new theoretical framework for quantifying heterogeneous sulfate production pathways in Beijing haze using field-based measurements of mass independent compositions of oxygen isotopes ($\Delta^{17}\text{O}$) in sulfates. The dataset is the first measurement of $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ in fine particles in the megacity Beijing. In addition, a combination of metastable and stable states was proposed to calculate the aerosol acidity, which plays a predominant role in the relative contributions of O_2 and NO_2 oxidation pathways. The sulfate formation in Beijing haze is a subject of intense scrutiny in recent years in atmospheric chemistry community, and the use of triple oxygen isotopic analysis for such quantification is a large step forward in this field. The isotopic measurements made in UW are of high quality as usual. Some uncertainties exist in calculation and deserve further assessment, but given that this is a first investigation and the manuscript is thorough and interesting, I strongly recommend publication in ACP after considering the following comments and suggestions.

Response: Thanks for your comments. We reply to your comments one by one as follows:

Major comments:

1. **Q:** In this manuscript, there is a big assumption that the $\Delta^{17}\text{O}$ of sulfates produced by the NO_2 oxidation is zero. I think the authors are probably right, but there remain uncertainties because the NO_2 oxidation mechanism has not yet been defined. In the introduction, the authors cited the work of Shen and Rochelle (1998) who proposed a radical chain reaction. In this case, I agree that the sulfate product is normal. In the other work cited by the author (He et al., 2014), it was proposed that oxygen is a key oxidant and oxygen atom transfer from O_2 to SO_4^{2-} via NO_2 . The conclusion made by He et al. (2014) is based on a set of laboratory experiments, in which sulfates would not produce without O_2 . However, in their experiments, the role of O_3 was not examined. In the ambient atmosphere (especially in urban areas), the reaction $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ cannot be ignored. Although it was argued that O_3 was not important in Beijing haze because of its low mixing ratio, is it possible that the low O_3 mixing ratio is a result of enhanced $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ reaction (aka “titration effect”)? As shown in many studies (e.g., Xu et al., 2011; Zhang et al., 2015), ozone mixing ratios in the urban region are lower than the surrounding rural region (probably in part due to large local emissions of fresh NO in the urban region). In this case, the oxygen anomaly in ozone molecules would lead to positive $\Delta^{17}\text{O}$ values in sulfates produced via the NO_2 oxidation. Because of the enriched ^{17}O in ozone, a small fraction can lead to a non-zero $\Delta^{17}\text{O}$ in the sulfate product. In addition, $\text{NO} + \text{HO}_2 \rightarrow \text{OH} + \text{NO}_2$ is also a possible pathway to transfer anomalous oxygen atoms (with the assumption that $\Delta^{17}\text{O}$ in HO_2 is non-zero based on $\Delta^{17}\text{O}$ values in H_2O_2). Can the authors provide a quantitative estimation on the possible contribution of O_3/HO_2 to the NO_2 oxidation? Because the validity of this assumption can significantly alter the conclusion of this paper and there is no laboratory experiment to support this assumption at present, I think such discussion would make the authors’ case stronger.

A: Thanks for your comments. In the work of He et al. (2014), they stated in their paper that “As shown in Fig. 2, sulfate can be formed on the CaO surface only in the presence of O₂. Similar phenomena were also found on Al₂O₃, ZnO, and TiO₂ surfaces (see Supplementary Information). Therefore, O₂ was the key oxidant in the process of SO₂ oxidation”. This statement should be reliable as it is what’s shown in Fig. 2 of their work (this figure is presented below for convenience). But I think the mechanism of SO₂ oxidation proposed by them is contradictory to this figure. In their proposal, the mechanism of SO₂ oxidation has two steps, the first one is (SO₂+2NO₂+M→M–SO₄+2NO) and the second one is (2NO+O₂+M→2NO₂). It should be noted that SO₄²⁻ is thought to form in the first step of their proposed mechanism, with two oxygen-atom directly from NO₂ without O₂. If this mechanism is correct, we expect SO₄²⁻ being seen when SO₂+NO₂ is exposed to the surface of CaO. However, in their laboratory experiments, when they continuously exposed SO₂+NO₂ to the surface of CaO, SO₄²⁻ was not observed at all (see black solid squares in Fig. 2 of their work). Therefore, I think the two-steps oxidation mechanism that they proposed to explain the experimental results in their study is problematic. One more piece of evidence supports our speculation and is shown in Fig. 1B of their work (this figure is also presented below for convenience). Sulfite but not sulfate is observed when they exposed SO₂ to the surface of CaO, which means one oxygen-atom from H₂O is transferred to sulfite. SO₄²⁻ was not observed when it was exposed only to NO₂ but was observed when continually exposed to NO₂+O₂, again suggesting that the oxygen-atom cannot be directly transferred from NO₂ but from O₂. In summary, in the oxidation of SO₂ to SO₄²⁻, one oxygen-atom is transferred from H₂O to form S(IV) (= SO₂ H₂O+HSO₃⁻+SO₃²⁻), the other is from O₂ but not via NO₂ based on the experimental results of He et al. (2014). As for the specific mechanism for SO₂+NO₂+O₂ in the experiments of He et al. (2014), it may be similar (but different) to the proposed mechanism by Clifton et al. (1988). In the work of Clifton et al. (1988), the oxidation mechanism of S(IV) by NO₂ in bulk solution was proposed as follows:



Similarly, we propose the experimental results in the work of He et al. (2014) can be explained as follows: when SO₂ is exposed the surface of CaO, sulfite formed (Fig. 1B of their work). In the presence of NO₂, sulfite may react with NO₂ to form an addition complex (e.g., (O₂N–SO₃–NO₂)²⁻), so SO₄²⁻ is not observed (black solid squares in Fig. 2 of their work). In the presence of O₂, the formed addition complex may react with O₂ (or oxygen radicals induced by O₂, e.g., O₂⁻, O⁻) to form SO₄²⁻ (red hollow squares in Fig. 2 of their work). So even though we agree with the experimental results of He et al. (2014) that “O₂ was the key oxidant in the process of SO₂ oxidation”, we think the oxygen-atom transfer from O₂ may be via an addition complex but not via NO₂. It’s worth noting that the proposed oxidation mechanism for S(IV)+NO₂, no matter via a radical chain mechanism (Shen and Rochelle, 1998) or via oxygen-atom transfer from OH⁻ (Clifton et al., 1988) or via oxygen-atom transfer from O₂ in our proposal based on experimental results of He et al. (2014), all result in Δ¹⁷O(SO₄²⁻) =

0 ‰. So based on information available in literature, we think it's appropriate to assume $S(IV)+NO_2$ leads to $\Delta^{17}O(SO_4^{2-}) = 0 ‰$. Therefore we describe this as “Sulfate produced by NO_2 oxidation is suggested to occur either via a radical chain mechanism (Shen and Rochelle, 1998), via oxygen-atom transfer from OH^- (Clifton et al., 1988), or from O_2 based on experimental results of He et al. (2014), resulting in $\Delta^{17}O(SO_4^{2-}) = 0 ‰$ ” in lines 74–76 of the present manuscript.

Since it is not oxygen in NO_2 that is directly transferred to sulfate, the role of O_3/HO_2 in NO oxidation is irrelevant in this case.

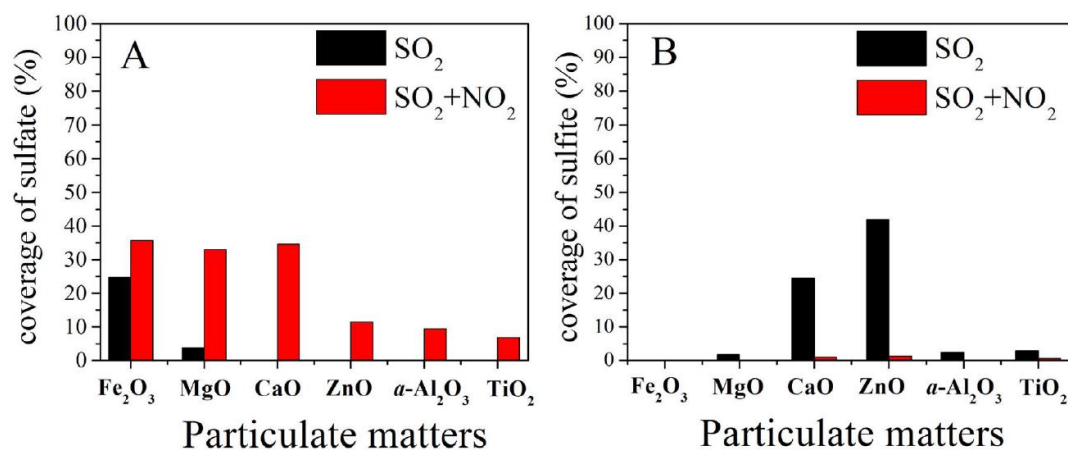


Figure 1 | Surface coverage of (A) sulfate and (B) sulfite species on mineral oxides after heterogeneous reaction of SO_2 or SO_2+NO_2 for 2 h. Reaction conditions: carrier gases: $N_2(80\%) + O_2(20\%)$ with total flow of 100 mL/min; concentrations of SO_2 and NO_2 : both 200 ppm; $T = 303$ K. A synergistic effect between SO_2 and NO_2 was also observed when reactant concentrations were at ppb level with long reaction time (see Supplementary Information).

Figure 1 of the work of He et al. (2014).

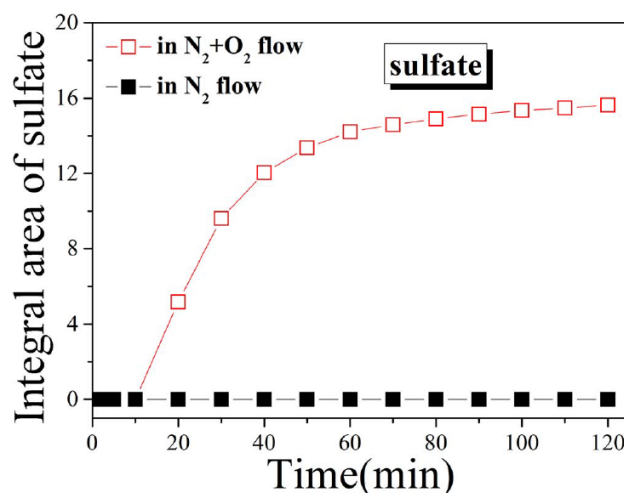


Figure 2 | Comparison of integral infrared peak area of sulfate when NO_2+SO_2 was exposed to the surface of CaO with pure N_2 (black solid squares) and synthetic air ($80\%N_2+20\%O_2$) (red hollow squares) as carrier gas. Reaction conditions: total flow = 100 mL/min; concentrations of SO_2 and NO_2 both 200 ppm; $T = 303$ K.

Figure 2 of the work of He et al. (2014).

2. **Q:** The calculation of pH is a little bit outside of my area of expertise, but I think the authors did a good job of discussing uncertainties and caveats, and the calculation of metastable/stable states proposed by the authors seems scientifically sound. My only concern is the discussion of NO_2/O_2 oxidation pathways (Lines 341-369). I understand the authors want to convince readers that the NO_2 oxidation could be potentially important. However, as noted by the authors,

the estimated production rate of O₂ oxidation is ~4 orders of magnitude greater than P_{het} (lines 358-369). Therefore, a very small fraction of aerosols with pH < 3 seems enough to explain the heterogeneous production rate via O₂ oxidation. In this case, why do we need the NO₂ oxidation? I would like to see discussion why O₂ oxidation cannot explain the heterogeneous formation here and why NO₂ oxidation is required. I think discussing the O₂ oxidation first and then the NO₂ oxidation would make this part easier to read and follow.

A: Thanks for your affirmations and comments. One of our points is that NO₂ and O₂ oxidation pathways may co-exist in ambient atmosphere due to the heterogeneity of aerosol state and pH. Therefore, we discussed that at different conditions the importance of NO₂ or O₂ oxidation pathway in heterogeneous sulfate production varies. In our discussion, we attempted to pay equal attention to these two pathways. As you know, however, no other experimental results about SO₂ oxidation by O₂ on acidic microdroplets have been published yet beyond the pioneering work of Hung and Hoffmann (2015), so we have little information about this pathway. Hung and Hoffmann (2015) reported the maximum of the reaction rate of O₂ oxidation on acidic microdroplets at pH ≤ 3 and suggested that it decreased with increasing pH when pH > 3 without reporting its specific value. However, the aerosol pH calculated by ISORROPIA II is far larger than 3 (7.6 ± 0.1 for stable state assumption and 4.7 ± 1.1 for metastable state assumption), so we cannot figure out its production rate but calculate its maximum value by using reaction rate at pH ≤ 3, and we use this maximum to see if it can meet our calculated P_{het} . The estimated maximum of $P_{\text{het, S(IV)+O}_2}$ is four orders of magnitude larger than P_{het} , which is too high. But, on the other hand, we note that in the work of He et al. (2014), SO₄²⁻ was not seen when SO₂+O₂ was exposed on most mineral oxides (Fig. 1A of their work) and in the work of Wang et al. (2016), they found SO₂ oxidation by O₂ was negligible in ammonium solution. These two works along with the work of Hung and Hoffmann (2015) directly suggest O₂ oxidation pathway may be negligible at higher pH conditions. Since we cannot quantify the fraction of aerosols with pH ≤ 3 (Kelvin effect) and even cannot verify their existence in the ambient atmosphere during Beijing haze, we realize that the uncertainty of estimating the production rate of O₂ oxidation pathway is far larger than NO₂ oxidation pathway. Based on this situation, we first discussed the NO₂ oxidation pathway and when NO₂ oxidation was not high enough to meet P_{het} , we further examined O₂ oxidation on acidic microdroplets. To better remind readers of the uncertainty of estimating O₂ oxidation pathway in the present manuscript, we described “This value should be an overestimate due to our calculated bulk aerosol pH predicted in metastable state being (4.4 ± 0.6) during PD and the experimental results of He et al. (2014) and Wang et al. (2016) suggests O₂ oxidation pathway is negligible at higher pH conditions (e.g., on CaO and in NH₄⁺ solution)” in lines 369–372. In summary, we think NO₂/O₂ oxidation pathways should be paid equal attention to. The order of discussing NO₂ oxidation first and then O₂ oxidation in our present scenario is based on the consideration that there exists larger uncertainty of estimating production rate of O₂ oxidation pathway due to less information about this pathway. So more studies about SO₂ oxidation by O₂ on acidic microdroplets proposed by Hung and Hoffmann (2015) need to be done in the future.

Specific comments:

1. **Q:** Line 24: Please give a quantitative context here (48±5%). The manuscript is focused on the heterogeneous sulfate production and therefore it is important to let readers know its overall contribution.

A: Thanks for this suggestion. This information has been given in lines 24–26 now, it reads “However, heterogeneous sulfate production (P_{het}) on aerosols was estimated to dominate sulfate formation during PD of other cases, with a fractional contribution of (48±5) %.

2. **Q:** The introduction could be better constructed. As noted by the authors, the relative importance of O_2 and NO_2 oxidation pathways is highly depending on pH and is difficult to constrain (lines 60-62). In lines 76-77, the authors state that the relative importance of different sulfate formation pathways is quantified in this study. So when I read this part, I thought the authors successfully solved this problem. However, this is not the case. I think the major advantage of $\Delta^{17}\text{O}$ in this study is to constrain the O_3 oxidation pathway in heterogeneous sulfate formation, which is of large uncertainties in previous studies. This should be highlighted. In the end of introduction, it's better to explicitly state something like “the contributions of O_3 and H_2O_2 oxidation in heterogeneous sulfate formation are quantified, and the roles of NO_2/O_2 oxidation are discussed.” To prevent any overstatement.

A: Thanks for your suggestions. We added “Laboratory work has suggested SO_2 oxidation by O_3 on mineral dust is a significant pathway for sulfate production (Li et al., 2006), but its role in Beijing haze has not been determined.” in lines 57–58 to pave the way for the following discussion. Based on your suggestions, we also state that “In this work, first observations of $\text{PM}_{2.5}$ $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ during haze events from October 2014 to January 2015 in Beijing are reported, contributions of O_3 and H_2O_2 oxidation in heterogeneous sulfate formation are quantified, and the roles of NO_2 and O_2 oxidation are explored.” in lines 78–80 to prevent any overstatement.

3. **Q:** Lines 255-256: A recent study reported one-year $\Delta^{17}\text{O}$ measurements in sulfates collected from a background mountain site in East China (Lin et al., 2017). This work is closely connected to the subject of the manuscript and should be cited.

A: Thanks for your recommendation. This important work has been cited in line 260 now.

4. **Q:** Lines 259-260 and Fig. 2: This part is not clear to me. Do the authors mean that the $\Delta^{17}\text{O}$ is directly linked to the $\text{O}_3/\text{H}_2\text{O}_2$ concentrations? If this is the case, scatter plots (with correlation coefficients) or time series may be clearer. I am also confused why cases I and II were grouped together. In the rest part of this manuscript (e.g., abstract and Figure 5), case II seems significantly different from other cases. And where is case V? Please clarify. In addition, it is better to use “calculated H_2O_2 ” as the y-axis title of Fig. 2c.

A: Thanks for your comments. The objective of this part is to see whether the observed results “the NPD to PD difference of $\Delta^{17}\text{O}_{\text{obs}}$ can be case-dependent.” is roughly linked to some easily observed or estimated parameters (e.g., observed O_3 and calculated H_2O_2). We agree that “scatter plots (with correlation coefficients) or time series may be clearer”,

so we grouped the time series of observed O_3 and calculated H_2O_2 in Fig. 1c and removed the former Fig. 2. We also show the scatter plots with correlation coefficients below (Fig. C1) for your review. For your concern about why we group Cases I and II together and Cases III to V together in the former Fig. 2, we do so based on two reasons. The first reason is the phenomenon that $\Delta^{17}O_{obs}$ increased from NPD to PD during Case I and II while the opposite trend was observed for Case III to V (Fig. 1b). The second reason is that Case I and II is in autumn without centralized heating while Case III to V is during the heating season in Beijing. In addition, we did show the data of Case V in the former Fig. 2, I think you may not notice the x-axis title in the right part of former Fig. 2, which reads “Case III to V”, or I may misunderstand your comment. As you suggested, we used “calculated H_2O_2 ” as the y-axis title of Fig. 1c in the present manuscript.

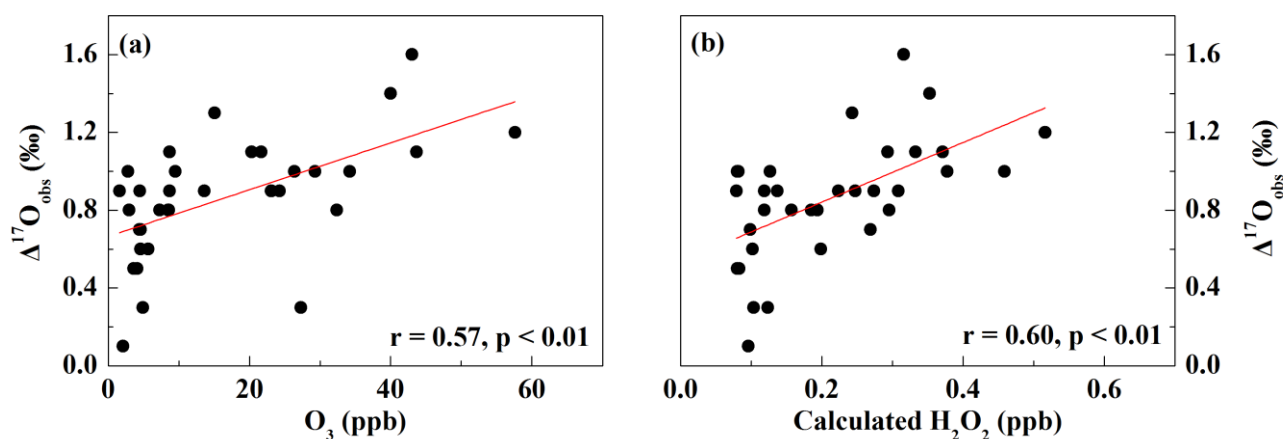


Figure C1. The relationship between O_3 and $\Delta^{17}O_{obs}$ (a) and relationship between calculated H_2O_2 and $\Delta^{17}O_{obs}$ (b). The red lines are linear least-squares fitting lines.

5. **Q:** Line 263: What is “the range of any single reaction pathway”? It is not clear to me. I don’t think this statement is exactly correct. For example, a sample with $\Delta^{17}O$ ranging from 0.6 to 1 per mil could be 100% produced from the H_2O_2 oxidation because $\Delta^{17}O$ values in H_2O_2 are in the range of 1.2-2 per mil. The observed $\Delta^{17}O$ value is not a supportive evidence for this statement.

A: Thanks for noticing this. We realize this statement is not exactly correct and have removed it now.

6. **Q:** Lines 274-276: Why did the author look at the $PM_{2.5}$ instead of sulfate concentration? I think a good correlation between P_{het} and sulfate concentrations would be more convincing. From Figure 5, it seems that the variation of SO_4^{2-} is more correlated to P_{cloud} than P_{het} . The similarity of $\Delta^{17}O_{cloud}$ and $\Delta^{17}O_{obs}$ in Figure 6 also likely indicates that the contribution of P_{cloud} is more dominant than P_{het} . If this is the case, the role of P_{het} may be overstated. I would like to see a table showing the percentages of P_{het} , P_{cloud} and P_{OH} in each case.

A: Thanks for your comments. We look at the relationship between $PM_{2.5}$ concentration and P_{het} instead of sulfate with P_{het} in former Fig. 4b of our former manuscript due to that we want to examine P_{het} variations during the evolution of haze pollution, where haze events are defined based on $PM_{2.5}$ concentrations. Based on your suggestions, we removed the relationship between $PM_{2.5}$ and P_{het} and show the time series of P_{het} along with SO_4^{2-} concentrations in present Fig. 3b (also

shown as below). It's clear in Fig. 3b that P_{het} shows very similar trends with SO_4^{2-} concentrations except for Case II, in which sulfate production was found to predominantly occur by in-cloud reactions. Generally, the variation of SO_4^{2-} along with P_{cloud} is not as good as that with P_{het} (Fig. C2) in our estimate. The estimated fractional contribution of different pathways is shown in Table C1 (also shown as Table S7 in SI). The f_{het} and f_{cloud} during polluted days in Case II is respectively 23 % and 68 % while f_{het} and f_{cloud} is respectively (48±5) % and (38±7) % in Case I and III to V, so I think it's not inappropriate to state that heterogeneous reactions were found to dominate sulfate formation in four out of the total five cases. For the similarity between $\Delta^{17}\text{O}_{\text{cloud}}$ and $\Delta^{17}\text{O}_{\text{obs}}$ ($r = 0.63$, $p < 0.01$), I think it mainly suggests that our estimate of in-cloud reactions should be reliable.

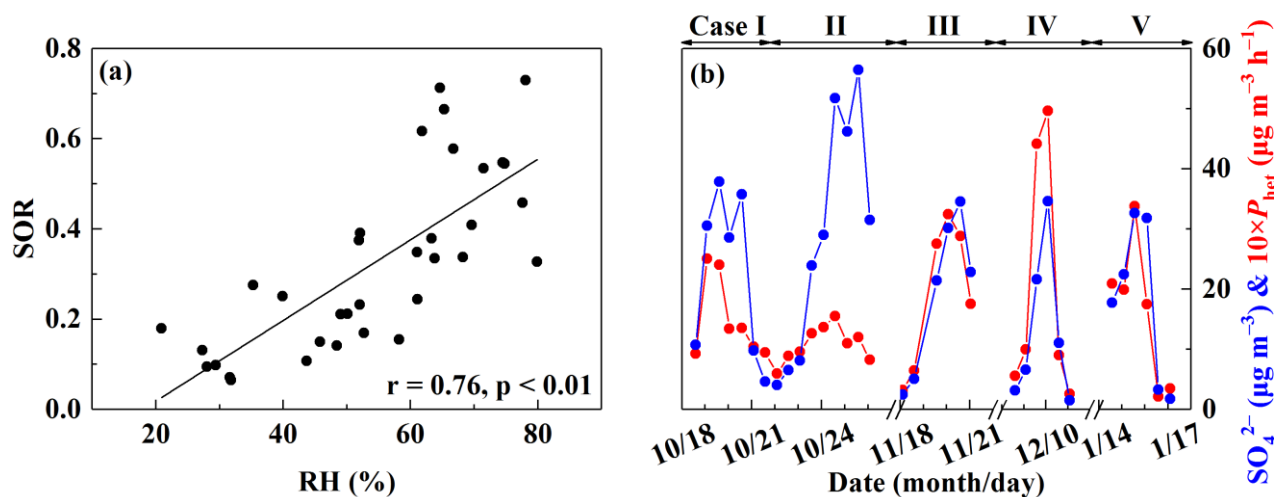


Figure 3 in the main text. The relationship between RH and SOR (a) and time series of overall heterogeneous sulfate production (P_{het}) along with SO_4^{2-} concentrations (b). The black line in (a) is linear least-squares fitting line.

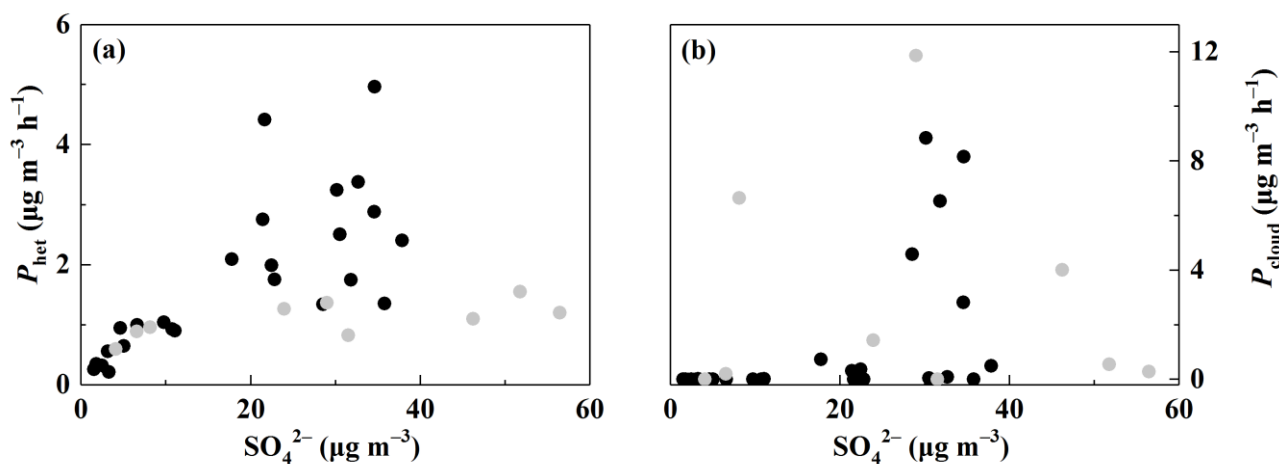


Figure C2. Scatter plots of P_{het} (a) and P_{cloud} (b) with SO_4^{2-} . The light gray dots are during Case II.

Table C1. Estimated fractional contribution of different sulfate production pathways during Beijing haze.

Case	f_p (%) ^a	f_{het} (%)	f_{cloud} (%)	$f_{\text{SO}_2+\text{OH}}$ (%)
I	9	54	29	8
II	6	23	68	3

III	11	42	46	1
IV	15	47	37	1
V	9	49	41	1

^a f_p , f_{het} , f_{cloud} , and f_{SO_2+OH} respectively represents fractional contribution from primary sulfate, heterogeneous reactions, in-cloud reactions and gas-phase pathway.

7. **Q:** Lines 284-286: In Figure 5, the peak of P_{cloud} is at 10/24, not exactly matching the SO_4^{2-} peak at 10/25. Could the authors discuss about this difference? Is it because of a stagnant meteorological condition? Or is it possible that the P_{cloud} was underestimated?

A: Thanks for your comment. Previous studies have suggested the stagnant meteorological condition is a key factor in the formation of haze in winter Beijing (Zheng et al., 2015), however, its role has not been quantified yet. For the reasons for the phenomenon that the peak of P_{cloud} is not exactly matching SO_4^{2-} peak at 10/25, in addition to the stagnant meteorological condition as you comment, another reason may be that the large mass of sulfate produced in cloud needs to accumulate to lead to the peak of surface SO_4^{2-} . It could be possible that in-cloud reactions were underestimated; however, previous work by Wang et al. (2014) using a global model showed that biases in meteorology, including biases in clouds, cannot explain the models underestimate of sulfate production rates during a Beijing haze event.

8. **Q:** Line 371-372: Please give a quantitative context as suggested before.

A: Thanks for this suggestion. A quantitative context has been added, it reads “Our study suggests that both in-cloud reactions and heterogeneous reactions can dominate sulfate formation during Beijing haze, with the fractional contribution of $f_{cloud} = 68\%$ in Case II and $f_{het} = (48 \pm 5)\%$ in Case I and III–V” in lines 376–377.

Typos:

9. **Q:** Line 84: “around”

A: Thanks for noticing this. The word “round” has been changed into “around” and the missing space has been added in line 87.

10. **Q:** Line 149: “sulfate formation”

A: Thanks for noticing this. The missing space between “sulfate” and “formation” has been added in line 154.

11. **Q:** Line 282: “cases”

A: Thanks for noticing this. The word “Cases” has been changed into “cases” in line 286.

12. **Q:** There are many spaces missing in the manuscript. I am not going to go through all of them.

A: Thanks for noticing this. We are very sorry that many spaces missed when we use another computer to edit and upload the document in final. We added all the missing space in the present manuscript.

References

- Clifton, C. L., Altstein, N., and Huie, R. E.: Rate constant for the reaction of nitrogen dioxide with sulfur (IV) over the pH range 5.3-13, *Environ. Sci. Technol.*, 22, 586-589, 1988.
- He, H., Wang, Y., Ma, Q., Ma, J., Chu, B., Ji, D., Tang, G., Liu, C., Zhang, H., and Hao, J.: Mineral dust and NO_x promote the conversion of SO₂ to sulfate in heavy pollution days, *Sci. Rep.*, 4, 4172, 2014.
- Hung, H.-M., and Hoffmann, M. R.: Oxidation of gas-Phase SO₂ on the surfaces of acidic microdroplets: Implications for sulfate and sulfate radical anion formation in the atmospheric liquid phase, *Environ. Sci. Technol.*, 49, 13768-13776, 2015.
- Li, L., Chen, Z., Zhang, Y., Zhu, T., Li, J., and Ding, J.: Kinetics and mechanism of heterogeneous oxidation of sulfur dioxide by ozone on surface of calcium carbonate, *Atmos. Chem. Phys.*, 6, 2453-2464, 2006.
- Shen, C. H., and Rochelle, G. T.: Nitrogen dioxide absorption and sulfite oxidation in aqueous sulfite, *Environ. Sci. Technol.*, 32, 1994-2003, 1998.
- Wang, G., Zhang, R., Gomez, M. E., Yang, L., Zamora, M. L., Hu, M., Lin, Y., Peng, J., Guo, S., and Meng, J.: Persistent sulfate formation from London Fog to Chinese haze, *P. Natl. Acad. Sci. USA*, 113, 13630-13635, 2016.
- Wang, Y., Zhang, Q., Jiang, J., Zhou, W., Wang, B., He, K., Duan, F., Zhang, Q., Philip, S., and Xie, Y.: Enhanced sulfate formation during China's severe winter haze episode in January 2013 missing from current models, *J. Geophys. Res.*, 119, 10425-10440, 2014.
- Zheng, B., Zhang, Q., Zhang, Y., He, K., Wang, K., Zheng, G., Duan, F., Ma, Y., and Kimoto, T.: Heterogeneous chemistry: a mechanism missing in current models to explain secondary inorganic aerosol formation during the January 2013 haze episode in North China, *Atmos. Chem. Phys.*, 15, 2031-2049, 2015.