## **Comments and Responses**

Referee #1

**Comments:** In the manuscript, the study reported the first observations of PM2.5\_ $\Delta^{17}O(SO_4^{2-})$  during haze events from October 2014 to January 2015 in Beijing, and use them to quantify the relative importance of different sulfate formation pathways, which is quite interesting and significant. But there are some mistakes and problem:

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

1. **Q:** There are some typesetting in the manuscript: such as: (1) line 1: should be sulfate production; (2) line 25: formationwith should be formation with;(3) line 30: should be  $NO_2$  in; (4) line 84: should be round 20m; (5) line 84: should be round 60m; line 243: should be Figure 1a shows;

A: Thanks for noticing these mistakes. Some typesetting problems occurred when we used another computer to edit and upload the document in final. We corrected all the typesetting problems you mentioned. The corrected typesetting is respectively in line 1 for "sulfate production", in line 30 for "NO<sub>2</sub> in", in line 87 for "around 20 m", in line 87 for "around 60 km" and in line 248 for "Figure 1a shows".

2. **Q:** Sampling site locate at a country-site (is not downtown), round 60 km northeast of downtown, and so that it is not perfect to know isotopic constraints on heterogeneous sulfate production in Beijing haze, the reason is that downtown has more information about the automobile exhaust emission, enterprise emission, and resident emission and so on. Furthermore, the sampling site is close to Yanxi lake, so that it has been probably affected by cloud liquid water content;

A: Thanks for your comments. For your concern about the sampling site, we do agree that it would be better if the sampling site was in downtown area. However, we think our sampling site is a representative site of Beijing haze for the following reasons:

(1) High concentrations of both secondary and primary air pollutants were observed at our sampling site. Figure 1 in the main text shows that 12h-averaged  $SO_4^{2-}$  concentrations at our sampling site can be up to 56.4 µg m<sup>-3</sup>. The 1h-averaged concentrations of primary air pollutants such as CO at our sampling site can be as high as 4025 ppb (Fig. C1), and shows similar trends and range with observations at the nearest station (Huairou station) set for estimating urban environment by (BJMEMC, Beijing Municipal Environmental Monitoring Center http://zx.bjmemc.com.cn/getAqiList.shtml?timestamp=1513326206397). For other air pollutants that were not observed at our sampling site but observed at BJMEMC stations (e.g., PM<sub>2.5</sub>, SO<sub>2</sub> and NO<sub>2</sub>), the comparisons between observations at Huairou station and a downtown site (Tiantan station, Fig. C2) show that the variations and range of PM<sub>2.5</sub> and SO<sub>2</sub> are very similar in these two sites. We also note that the peak concentrations of CO and  $NO_2$  at or around our sampling site are generally lower than those observed at Tiantan station, so we do agree as you comment "downtown has more information about the automobile exhaust emission, enterprise emission, and resident emission and so on". However, our sampling site is suggested to be a suburban site based on the above comparisons and other studies (Wang et al., 2016a; Wang et al., 2017; Li et al., 2017; Tong et al., 2015).

(2) Our sampling site is usually downwind of downtown Beijing during polluted days (PD,  $PM_{2.5} > 75 \ \mu g \ m^{-3}$ ). Backward trajectory analysis shows that air masses from downtown Beijing can reach our sampling site within a day during PD (Fig. C3), which suggests our sampling site can reflect the main signal of downtown Beijing, especially considering the lifetime of sulfate which is 4–5 days (Alexander et al., 2012).

(3) The total area of Beijing is around 16411 km<sup>2</sup> while its urban area is only about 1401 km<sup>2</sup>. As haze in Beijing and North China Plain is a regional phenomenon (Zheng et al., 2015), it's truly important to sample at downtown area, however, it may be also necessary to sample at suburban area to have a more comprehensive understanding of Beijing haze.

(4) Our sampling site at UCAS (University of the Chinese Academy of Sciences) is a supersite set by HOPE-J<sup>3</sup>A (Haze Observation Project Especially for Jing-Jin-Ji Area). Other observations at this site have been used to discuss scientific problems in Beijing haze in previous studies, e.g., (Zhang et al., 2017; Xu et al., 2016; Chen et al., 2015; Tong et al., 2015). Especially, in the work of Tong et al. (2015), they found that the heterogeneous reaction efficiency from NO<sub>2</sub> to HONO is higher in suburban areas than urban areas. As our sampling site is the same as the suburban site in the work of Tong et al. (2015), we think our sampling site should be suitable, even though it may be not perfect, to discuss heterogeneous sulfate production in Beijing haze.

(5) It's true that our sampling site is close to Yanqi lake (Fig. C2). The linear distance from our sample site to the nearest edge of Yanqi lake is around 1 km and is around 3 km to the farthest edge of Yanqi lake. We note that it's difficult to give an accurate estimate of the influence of Yanqi lake on cloud liquid water in the present study as the formation of cloud is quite complicated. However, as the area of Yanqi lake is about 2.3 km<sup>2</sup>, the area fraction of Yanqi lake to the nearest 3 km circular area from our sample site is about 8 % (= $2.3/(3.14 \times 3^2)$ ), which is small. So that we expect its influence on cloud liquid water is probably small, too, especially in winter when the lake is frozen.



**Figure C1.** Comparisons of air pollutants observed at our sampling site with that observed at Huairou station and Tiantan station. The Huairou station is the nearest station (to ours) set for estimating urban environment by Beijing Municipal Environmental Monitoring Center (BJMEMC), while the Tiantan station is located in the center of downtown Beijing (please refer to Fig. C2 as below). The missing concentrations of CO at our sampling site are due to that our CO analyzer (EC9830B, Ecotech Inc., Australia) were taken way to be calibrated. Hourly concentrations of other air pollutants (e.g., PM<sub>2.5</sub>, SO<sub>2</sub> and NO<sub>2</sub>) were not observed at our sampling site but observed at BJMEMC stations.



Figure C2. Map of our sampling site. The blue area on the base map represents rivers and lakes with a map scale of 1:1250000.



Figure C3. 1-day backward trajectories reaching our sampling site at each hour during our sampling time when  $PM_{2.5} \ge 75$  µg m<sup>-3</sup>.

3. **Q:** Method: As we know, these data are likely contaminated to various degrees by occluded nitrate isotope signal in the samples, so that we had better remove nitrate during the preparing the  $Ag_2SO_4$ , but the manuscript has not removed the nitrate, which will effect on the sulfur isotope composition results;

A: Thanks for your comment. Actually, we removed NO<sub>3</sub><sup>-</sup> before SO<sub>4</sub><sup>2-</sup> being converted to Ag<sub>2</sub>SO<sub>4</sub>. The preparation and measurements of  $\Delta^{17}O(SO_4^{2-})$  in the University of Washington have been well documented in previous studies (Geng et al., 2013; Chen et al., 2016; Alexander et al., 2012), thus we didn't describe the experimental procedures in detail in the former manuscript. Now, the description "SO<sub>4</sub><sup>2-</sup> was separated from other anions (e.g., NO<sub>3</sub><sup>-</sup>) by ion chromatography" is presented in lines 111–112.

## 4. Q: The manuscript should introduce name of laboratory, precision of the machine.

A: Thanks for your suggestions. The name of the laboratory where ions were measured now is added in lines 98–99 reading "The measurements of ions were conducted in Anhui Province Key Laboratory of Polar Environment and Global Change in University of Science and Technology of China". The description about precisions of ion measurements is added in lines 104–105 reading "Typical analytical precision by our instrument is better than 10 % RSD (relative standard deviation) for all ions (Chen et al., 2016)". The name of the laboratory where our  $\Delta^{17}O(SO_4^{2-})$  was measured now is added in lines 105–107 reading "The preparation and measurements of  $\Delta^{17}O(SO_4^{2-})$  were conducted in Isolab (https://isolab.ess.washington.edu/isolab/) at the University of Washington, USA". The precision is dependent on the instrument itself and the method. The description about precision of our  $\Delta^{17}O(SO_4^{2-})$  measurements (which includes the machine MAT253) now is added in lines 116–118 reading "The precision of  $\Delta^{17}O$  measurements in our method is ±0.3 ‰ based on replicate analysis of standards, which is consistent with previous studies (Alexander et al., 2005; Sofen et al., 2014; Chen et al., 2016)".

## 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 ( $\Delta^{17}$ O) in sulfates. The dataset is the first measurement of  $\Delta^{17}$ O(SO<sub>4</sub><sup>2-</sup>) 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<sub>2</sub> and NO<sub>2</sub> 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:

**O:** In this manuscript, there is a big assumption that the  $\Delta^{17}$ O of sulfates produced by the NO<sub>2</sub> oxidation is zero. I think 1. the authors are probably right, but there remain uncertainties because the NO<sub>2</sub> 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<sub>3</sub> was not examined. In the ambient atmosphere (especially in urban areas), the reaction NO+O<sub>3</sub> $\rightarrow$ NO<sub>2</sub>+O<sub>2</sub> 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 NO+ $O_3 \rightarrow NO_2+O_2$  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  $\Delta^{17}$ O values in sulfates produced via the NO<sub>2</sub> oxidation. Because of the enriched <sup>17</sup>O in ozone, a small fraction can lead to a non-zero  $\Delta^{17}$ O in the sulfate product. In addition, NO+HO<sub>2</sub> $\rightarrow$ OH+NO<sub>2</sub> is also a possible pathway to transfer anomalous oxygen atoms (with the assumption that  $\Delta^{17}$ O in HO<sub>2</sub> is non-zero based on  $\Delta^{17}$ O values in H<sub>2</sub>O<sub>2</sub>). Can the authors provide a quantitative estimation on the possible contribution of  $O_3/HO_2$  to the NO<sub>2</sub> 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  $O_2$ . Similar phenomena were also found on  $Al_2O_3$ , ZnO, and TiO<sub>2</sub> surfaces (see Supplementary Information). Therefore,  $O_2$  was the key oxidant in the process of SO<sub>2</sub> 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 SO<sub>2</sub> oxidation proposed by them is contradictory to this figure. In their proposal, the mechanism of SO<sub>2</sub> oxidation has two steps, the first one is (SO<sub>2</sub>+2NO<sub>2</sub>+M $\rightarrow$ M–SO<sub>4</sub>+2NO) and the second one is (2NO+O<sub>2</sub>+M $\rightarrow$ 2NO<sub>2</sub>). It should be noted that SO<sub>4</sub><sup>2-</sup> is thought to form in the first step of their proposed mechanism, with two oxygen-atom directly from NO<sub>2</sub> without O<sub>2</sub>. If this mechanism is correct, we expect SO<sub>4</sub><sup>2-</sup> being seen when SO<sub>2</sub>+NO<sub>2</sub> to the surface of CaO. However, in their laboratory experiments, when they continuously exposed SO<sub>2</sub>+NO<sub>2</sub> to the surface of CaO. SO<sub>4</sub><sup>2-</sup> 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 SO<sub>2</sub> to the surface of CaO, which means one oxygen-atom from H<sub>2</sub>O is transferred to sulfite. SO<sub>4</sub><sup>2-</sup> was not observed when it was exposed only to NO<sub>2</sub> but was observed when continually exposed to NO<sub>2</sub>+O<sub>2</sub>, again suggesting that the oxygen-atom cannot be directly transferred from NO<sub>2</sub> but from O<sub>2</sub>. In summary, in the oxidation of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup>, one oxygen-atom is transferred from H<sub>2</sub>O to form S(IV) (= SO<sub>2</sub> H<sub>2</sub>O+HSO<sub>3</sub><sup>-+</sup>+SO<sub>3</sub><sup>2-</sup>), the other is from O<sub>2</sub> but not via NO<sub>2</sub> based on the experimental results of He et al. (2014). As for the specific mechanism for SO<sub>2</sub>+NO<sub>2</sub>+O<sub>2</sub> 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 NO<sub>2</sub> in bulk solution was proposed as follows:

$$2NO_{2}+SO_{3}^{2-} \rightarrow (O_{2}N-SO_{3}-NO_{2})^{2-}$$
$$(O_{2}N-SO_{3}-NO_{2})^{2-}+OH^{-} \rightarrow (HO-SO_{3}-(NO_{2})_{2})^{3-}$$
$$(HO-SO_{3}-(NO_{2})_{2})^{3-} \rightarrow 2NO_{2}^{-}+SO_{4}^{2-}+H^{+}$$

Similarly, we propose the experimental results in the work of He et al. (2014) can be explained as follows: when SO<sub>2</sub> is exposed the surface of CaO, sulfite formed (Fig. 1B of their work). In the presence of NO<sub>2</sub>, sulfite may react with NO<sub>2</sub> to form an addition complex (e.g.,  $(O_2N-SO_3-NO_2)^{2-}$ ), so  $SO_4^{2-}$  is not observed (black solid squares in Fig. 2 of their work). In the presence of O<sub>2</sub>, the formed addition complex may react with O<sub>2</sub> (or oxygen radicals induced by O<sub>2</sub>, e.g., O<sub>2</sub><sup>-</sup>, O<sup>-</sup>) to form  $SO_4^{2-}$  (red hollow squares in Fig. 2 of their work). So even though we agree with the experimental results of He et al. (2014) that "O<sub>2</sub> was the key oxidant in the process of SO<sub>2</sub> oxidation", we think the oxygen-atom transfer from O<sub>2</sub> may be via an addition complex but not via NO<sub>2</sub>. It's worth noting that the proposed oxidation mechanism for S(IV)+NO<sub>2</sub>, no matter via a radical chain mechanism (Shen and Rochelle, 1998) or via oxygen-atom transfer from OH<sup>-</sup> (Clifton et al., 1988) or via oxygen-atom transfer from O<sub>2</sub> leads to  $\Delta^{17}O(SO_4^{2-}) = 0$  ‰. So based on information available in literature, we think it's appropriate to assume S(IV)+NO<sub>2</sub> leads to  $\Delta^{17}O(SO_4^{2-}) = 0$  ‰. Therefore we describe this as "Sulfate produced by NO<sub>2</sub> oxidation is suggested to occur either via a radical chain mechanism (Shen and Rochelle, 1998), via oxygen-atom transfer from OH<sup>-</sup> (Clifton et al., 1988), or from O<sub>2</sub> based on experimental results of He et al. (2014), resulting in  $\Delta^{17}O(SO_4^{2-}) = 0$  ‰.

Since it is not oxygen in NO<sub>2</sub> 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<sub>2</sub> or SO<sub>2</sub>+NO<sub>2</sub> for 2 h. Reaction conditions: carrier gases:  $N_2(80\%) + O_2(20\%)$  with total flow of 100 mL/min; concentrations of SO<sub>2</sub> and NO<sub>2</sub>: both 200 ppm; T = 303 K. A synergistic effect between SO<sub>2</sub> and NO<sub>2</sub> 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<sub>2</sub> and NO<sub>2</sub> 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<sub>2</sub>/O<sub>2</sub> oxidation pathways (Lines 341-369). I understand the authors want to convince readers that the NO<sub>2</sub> oxidation could be potentially important. However, as noted by the authors, the estimated production rate of O<sub>2</sub> oxidation is \_4 orders of magnitude greater the  $P_{het}$  (lines 358-369). Therefore, a very small fraction of aerosols with pH<3 seems enough to explain the heterogeneous production rate via O<sub>2</sub> oxidation. In this case, why do we need the NO<sub>2</sub> oxidation? I would like to see discussion why O<sub>2</sub> oxidation cannot explain the heterogeneous formation here and why NO<sub>2</sub> oxidation is required. I think discussing the O<sub>2</sub> oxidation first and then the NO<sub>2</sub> oxidation would make this part easier to read and follow.

A: Thanks for your affirmations and comments. One of our points is that  $NO_2$  and  $O_2$  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 NO<sub>2</sub> or O<sub>2</sub> 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  $SO_2$  oxidation by O<sub>2</sub> 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  $O_2$  oxidation on acidic microdroplets at pH  $\leq$  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  $4.7 \pm 1.1$  for metastable state assumption), so we cannot figure out its production rate but calculate its maximum value by using reaction rate at pH  $\leq$  3, and we use this maximum to see if it can meet our calculated P<sub>het</sub>. The estimated maximum of  $P_{\text{het, S(IV)+O2}}$  is four order of magnitude larger than  $P_{\text{het}}$ , which is too high. But, on the other hand, we note that in the work of He et al. (2014), SO<sub>4</sub><sup>2-</sup> was not seen when SO<sub>2</sub>+O<sub>2</sub> was exposed on most mineral oxides (Fig. 1A of their work) and in the work of Wang et al. (2016b), they found  $SO_2$  oxidation by  $O_2$  was negligible in ammonium solution. These two work along with the work of Hung and Hoffmann (2015) directly suggest O<sub>2</sub> oxidation pathway may be negligible at higher pH conditions. Since we cannot quantify the fraction of aerosols with  $pH \leq 3$  (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 O<sub>2</sub> oxidation pathway is far larger than NO<sub>2</sub> oxidation pathway. Based on this situation, we first discussed the NO<sub>2</sub> oxidation pathway and when NO<sub>2</sub> oxidation was not high enough to meet  $P_{het}$ , we further examined O<sub>2</sub> 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  $(4.4\pm0.6)$  during PD and the experimental results of He et al. (2014) and Wang et al. (2016b) suggests O<sub>2</sub> oxidation pathway is negligible at higher pH conditions (e.g., on CaO and in NH<sub>4</sub><sup>+</sup> solution)" in lines 369–372. In summary, we think NO<sub>2</sub>/O<sub>2</sub> oxidation pathways should be paid equal attention to. The order of discussing NO<sub>2</sub> oxidation first and then O<sub>2</sub> oxidation in our present scenario is based on the consideration that there exists larger uncertainty of estimating production rate of  $O_2$ 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  $\Delta^{17}O$  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<sub>2</sub> oxidation by O<sub>3</sub> 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  $PM_{2.5} \Delta^{17}O(SO_4^{2-})$  during haze events from October 2014 to January 2015 in Beijing are reported, contributions of O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> oxidation in heterogeneous sulfate formation are quantified, and the roles of NO<sub>2</sub> and O<sub>2</sub> oxidation are explored." in lines 78–80 to prevent any overstatement.

3. **Q:** Lines 255-256: A recent study reported one-year  $\Delta^{17}$ 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  $\Delta^{17}$ O is directly linked to the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub>" 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  $\Delta^{17}O_{obs}$  can be case-dependent." is roughly linked to some easily observed or estimated parameters (e.g., observed O<sub>3</sub> and calculated H<sub>2</sub>O<sub>2</sub>). We agree that "scatter plots (with correlation coefficients) or time series may be clearer", so we grouped the time series of observed O<sub>3</sub> and calculated H<sub>2</sub>O<sub>2</sub> in Fig. 1c and removed the former Fig. 2. We also show the scatter plots with correlation coefficients below (Fig. C4) 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 C4.** 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<sub>2</sub>O<sub>2</sub> oxidation because  $\Delta^{17}$ O values in H<sub>2</sub>O<sub>2</sub> 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<sub>2.5</sub> 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<sub>4</sub><sup>2-</sup> 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. C5) 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  $\Delta^{17}O_{cloud}$  and  $\Delta^{17}O_{obs}$  (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<sub>4</sub><sup>2-</sup> concentrations (b). The black line in (a) is linear least-squares fitting line.



**Figure C5.** Scatter plots of  $P_{het}$  (**a**) and  $P_{cloud}$  (**b**) with SO<sub>4</sub><sup>2–</sup>. The light gray dots are during Case II.

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

Case	$f_{\mathrm{p}}\left(\% ight)^{\mathrm{a}}$	$f_{\rm het}(\%)$	$f_{\text{cloud}}(\%)$	$f_{\rm SO2+OH}$ (%)
Ι	9	54	29	8
II	6	23	68	3
III	11	42	46	1
IV	15	47	37	1
V	9	49	41	1

<sup>a</sup>  $f_p$ ,  $f_{het}$ ,  $f_{cloud}$ , and  $f_{SO2+OH}$  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<sub>4</sub><sup>2-</sup> 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  $f_{\text{cloud}} = 68\%$  in Case II and  $f_{\text{het}} = (48\pm5)\%$  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.

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