

## ***Interactive comment on “Isotopic constraints on heterogeneous sulphate production in Beijing haze” by Pengzhen He et al.***

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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 (D17O) in sulfates. The dataset is the first measurement of D17O(SO<sub>4</sub>) 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

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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.

Major comments:

1. In this manuscript, there is a big assumption that the D17O of sulfates produced by the NO<sub>2</sub> oxidation is zero. I think 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<sub>2</sub> to SO<sub>4</sub> via NO<sub>2</sub>. The conclusion made by He et al. (2014) is based on a set of laboratory experiments, in which sulfates would not produce without O<sub>2</sub>. 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>->NO<sub>2</sub>+O<sub>2</sub> cannot be ignored. Although it was argued that O<sub>3</sub> was not important in Beijing haze because of its low mixing ratio, is it possible that the low O<sub>3</sub> mixing ratio is a result of enhanced NO+O<sub>3</sub>->NO<sub>2</sub>+O<sub>2</sub> 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 D17O values in sulfates produced via the NO<sub>2</sub> oxidation. Because of the enriched 17O in ozone, a small fraction can lead to a non-zero D17O in the sulfate product. In addition, NO+HO<sub>2</sub>->OH+NO<sub>2</sub> is also a possible pathway to transfer anomalous oxygen atoms (with the assumption that D17O in HO<sub>2</sub> is non-zero based on D17O values in H<sub>2</sub>O<sub>2</sub>). Can the authors provide a quantitative estimation on the possible contribution of O<sub>3</sub>/HO<sub>2</sub> to the NO<sub>2</sub> oxidation? Because the validity of this

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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.

2. 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 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 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.

Specific comments:

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.

The introduction could be better constructed. As noted by the authors, the relative importance of O<sub>2</sub> and NO<sub>2</sub> 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 D17O in this study is to constrain the O<sub>3</sub> 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

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state something like "the 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>/O<sub>2</sub> oxidation are discussed." to prevent any overstatement.

Lines 255-256: A recent study reported one-year D17O 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.

Lines 259-260 and Fig. 2: This part is not clear to me. Do the authors mean that the D17O 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.

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 D17O ranging from 0.6 to 1 per mil could be 100% produced from the H<sub>2</sub>O<sub>2</sub> oxidation because D17O values in H<sub>2</sub>O<sub>2</sub> are in the range of 1.2-2 per mil. The observed D17O value is not a supportive evidence for this statement.

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> is more correlated to P(cloud) than P(het). The similarity of D17O(cloud) and D17O(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.

Lines 284-286: In Figure 5, the peak of P(cloud) is at 10/24, not exactly matching the SO<sub>4</sub> peak at 10/25. Could the authors discuss about this difference? Is it because of

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a stagnant meteorological condition? Or is it possible that the P(cloud) was underestimated?

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

Typos:

Line 84: “around”

Line 149: “sulfate formation”

Line 282: “cases”

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

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