Response to Reviewer#1's comments

General Comments:

In recent years, air pollution is seriously threatening the health of millions of people in China. Sulfate is one of the major chemical species in $PM_{2.5}$, and play a critical role in human health, and environmental chemistry. However, its formation in the atmosphere remains controversial. In this study, both observational data ($\delta^{34}S$ and $\delta^{18}O$ values) and laboratory simulation are used to constrain SO_2 oxidation pathways. The authors found that the sulfate in $PM_{2.5}$ was mainly formed from the oxidation of SO_2 by OH, H_2O_2 and TMI. This work provides a valuable dataset of $\delta^{34}S$ and $\delta^{18}O$ that add critical constraints for sulfate formation pathways.

Specific Comments:

1. Page 4, Lines 83-84 The authors mention that the sulfur isotopic fractionation factor of SO_2 oxidation by OH determined with laboratory experiments by Harris et al. (2012) was 1.0087. However, they discussed that "It is reported that sulfur isotope fractionation about SO_2 was -9‰ for homogeneous oxidation process (Tanaka et al., 1994)". The sulfur isotopic fractionation factor for homogeneous pathway (SO_2+OH) obtained by Tanaka et al. (1994) is different from the laboratory results by Harris et al. (2012). The authors need to compare these two values and explain which to be used for their discussion.

Response: Thanks for Reviewer's rigorous work. Harris et al. (2012) measured sulfur isotopic fractionation factor (αOH) of SO_2 oxidation by OH radicals, which was from the photolysis of water vapor at 30% relative humidity and 184.9 nm. They found that αOH was negatively correlated to the temperature and described as αOH=(1.0089±0.0007)−((4±5)×10^{-5})T (∘C). In the revised manuscript, we cancelled αOH values of SO_2 oxidation by OH, O_3/H_2O_2 and iron catalysis and emphasized their differences of αOH values.

In contrast, Tanaka et al. (1994) estimated αhom to be 0.991 during homogeneous oxidation of SO_2 by OH radicals by Ab initio calculations using transition state theory. The discrepancy between these two values may be explained by different research methods and/or temperature-dependence of fractionation factor. Generally, sulfate enriched light sulfur isotope (αhom<1) during SO_2 homogeneous oxidation for this process was only related to kinetic fractionation. Therefore, we used αhom=0.991 and αhet=1.0165 to study the contribution of SO_2 heterogeneous and homogeneous oxidation to sulfate in our study.

2. Page 17, lines 345-348 Their calculations displayed that the H_2O_2 pathway is predominated during heterogeneous oxidation of SO_2. Could the authors discuss the sources of H_2O_2 in atmosphere if it plays an important role in heterogeneous oxidation of SO_2?

Response: H_2O_2 production in the relatively clean atmosphere is ascribed to self-reaction of HO_2 radicals that mainly come from the reactions of OH with CO and volatile organic compounds. It is favorable for H_2O_2 formation under the conditions of high O_3 concentration, strong solar irradiation, and high temperature. We have added the sources of H_2O_2 in the revised manuscript.

3. The conclusion seems to be a bit dry. I suggest that the important implications for this work should be added, besides summarize the main points.

Response: This is a constructive suggestion, and we have added the following descriptions in Conclusions in the revised manuscript "Sulfur and oxygen isotopes can be used to gain an insight into sulfate formation. Sulfur isotope compositions in SO_2 and sulfate were simultaneously measured to quantify the contributions of SO_2 homogeneous and heterogeneous oxidation. Combining field observations of oxygen isotope in the atmosphere with the linear relationships of $\delta^{18}O$ values between H_2O and sulfate from different SO_2 oxidation processes can obtain an increased understanding of specific sulfate formation pathways. This study is favorable for deeply investigating sulfur cycle in the atmosphere".

Technical corrections:

4. Page 8, Line 163 Please change "The concentrations of $PM_{2.5}$, SO_4^{2-} and SO_2" to "Variations in concentrations of $PM_{2.5}$, SO_4^{2-} and SO_2".

Response: Thanks for Reviewer's suggestion. The sentence has been revised in the manuscript.

5. Page 9, Line 197 Please change "Sulfur isotope compositions in sulfate and SO_2" to "Variations in sulfur isotope compositions in sulfate and SO_2". In addition, the black solid circles represent the $\delta^{34}S$ values of sulfate instead of $PM_{2.5}$.

Response: Thanks for Reviewer's suggestion. The sentence has been revised in the manuscript. The black solid circles represent the $\delta^{34}S$ values of sulfate in $PM_{2.5}$, we have revised it in Fig.3.

Response to Reviewer#2's comments

This manuscript quantifies the sulfate formation pathways from 4 to 22 December 2019 in Nanjing by proposing a new method of simultaneously measuring sulfur and oxygen isotope compositions. The authors conclude that sulfate in $PM_{2.5}$ is mainly from a secondary source with SO_2 homogeneously oxidized by OH and heterogeneously oxidized by H_2O_2. Overall, the manuscript is well-written, and the method is reasonable. I have a few points that could be addressed to strengthen the manuscript and some minor comments.

General Comments:

1. The method seems applicable, but the authors need to explain the calculations better. I find it hard sometimes to understand how the result is derived. For example, the authors mentioned that the $\delta^{18}O$ value of primary sulfate is about 38 ‰ in Line 296 before they pointed out it was based on Formula (5). That is confusing. Why there are contribution ranges on each day in Table 1, instead of a single number like in Table 2?

Response: We are grateful for Reviewer's suggestions. We mentioned that $\delta^{18}O$ value of primary sulfate was about 38‰, which aimed to calculate the contribution of primary and secondary sulfate in the atmosphere. The $\delta^{18}O$ value of 38‰ was cited from the study of Holt and Kumar (1984), and it was not directly from Formula (5). We have added this reference in the revised manuscript.

In addition, we have further explained the calculation method about the contribution of primary and secondary sulfate in $PM_{2.5}$ and the ratios of different SO_2 oxidation pathways in the revised manuscript. We calculated the contribution of primary and secondary sulfate according to the equation: $\delta^{18}O_{PM_{2.5}}=\delta^{18}O_{PS}\times(1-f_{SS})+\delta^{18}O_{SS}\times f_{SS}$. It is known that 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 in this study. Therefore, the values of $\delta^{18}O_{SS}$ can be obtained based on the following three equations, respectively.

$\delta^{18}O_{SS}=0.69\times\delta^{18}O_{water}+9.5$ ‰ (OH)

$\delta^{18}O_{SS}=0.65\times\delta^{18}O_{water}+10.6$ ‰ (Fe^{3+}/O_2)

$\delta^{18}O_{SS}=0.43\times\delta^{18}O_{water}+12.5$ ‰ (H_2O_2)

As a result, data ranges about the contribution of primary and secondary sulfate in $PM_{2.5}$ are presented

in the original manuscript. To keep consistent with the single ratios of SO_2 different oxidation pathways to sulfate in Table 2, we have calculated the average contribution of primary and secondary sulfate on each day in Table 1 in the revised manuscript.

2. Is it possible to add more data points in Figure 7? It seems three are not robust enough to rerive the linear relationships.

Response: When simulatively studying the linear relationship of $\delta^{18}O$ values between H_2O and sulfate from SO_2 oxidation by H_2O_2 and Fe^{3+}/O_2 in the lab, we selected three kinds of representative water including tap-water, lake water and rainwater. The results showed that the slopes of these two linear curves were 0.43 and 0.65, respectively, which can basically reflect the characteristics of SO_2 heterogeneous oxidation mechanisms by H_2O_2 and Fe^{3+}/O_2.

We fully agree with the reviewer, and will provide more data points to precisely study the correlation in the following experimental design.

Minor Comments:

3. Line 69: Define RH here instead of in Line 186.

Response: According to Reviewer's suggestions, we have defined RH as "relative humidity" in Line 69 and deleted "relative humidity" in Line 187 in the revised manuscript.

4. Line 98/320: I did not find references related to Holt et al.

Response: We are very sorry for our negligence. The reference has been added in the revised manuscript. Holt, B.D. and Kumar R.: Oxygen-18 study of high-temperature air oxidation of SO_2, Atmos. Environ., 18, 2089-2094, https://doi.org/10.1016/0004-6981(84)90194-X, 1984.

5. Line 168-170: I am not sure why high CO is indicative of local emissions. It can be transported by a long range.

Response: As Reviewer said, CO can be transported by a long range due to its stability, and CO is not indicative of local emissions. In the manuscript, the conclusion "High CO concentration indicates that the pollution was mainly from local emissions" was mainly ascribed to the analysis of meteorological conditions. During the sampling period, the wind speed was lower than 3m/s and there was presence of

static weather. Therefore, it is hard for CO to transport a long range. We did not explain clearly in the original manuscript, and we have added the analysis of meteorological conditions in the revised one. The detailed description was as "Based on the wind speed was lower than 3m/s and there was presence of static weather during the sampling period, we believed that high CO concentration was mainly from local emissions.".

6. Line 192: What does the negative -2.9 mean here? Is it possible to have negative values?

Response: Thanks for Reviewer's suggestion. The negative -2.9 means that the lighter sulfur isotopes were enriched in SO_2. It is common to have negative $\delta^{34}S$ values in the samples.

7. Figure 3: Legend of $PM_{2.5}$ is wrong. Should be sulfate.

Response: We are very sorry for our cursoriness. The legend in Figure has been revised.

8. Line 249: The average of 51.6% seems just a little higher than 50%. I suggest to say that most of the days (seems 7 out of 11) have more than 50% contributions from heterogeneous oxidation.

Response: Thanks for Reviewer's suggestion. The sentence in the manuscript has been revised.

Page 11, Line 249-251: It is observed from Fig. 6 that most of the days (7 out of 11) have more than 50% contributions from SO_2 heterogeneous oxidation, which indicated that SO_2 heterogeneous oxidation was generally dominant during sulfate formation.

9. Figure 7: Are the three dots corresponding to three kinds of water? Better to describe it in the texts or figure title.

Response: Thanks for Reviewer's suggestion. Three dots are corresponding to three kinds of water in Fig.7, and we have made a detailed explanation as "which aims to make clear the relationship of $\delta^{18}O$ values between product sulfate and three kinds of water at 10 ℃" in Line 278 in the text.

10. Line 324: f_{SS-OH+} should be $f_{SS-OH}+$

Response: Thanks for Reviewer's suggestion. The formula has been revised in the manuscript.