Reviewer #2

It has been a long question regarding the origin(s) of the non-zero Δ17O (but also Δ33S and Δ36S values) observed in tropospheric aerosols. This study implements the four majors SO2 oxidation pathways into the GEOS-Chem model in clouds and on aerosols and compared with the sulfates measured in China (coupled with the O- isotopes). This study also discussed the contribution of the different oxidation path- ways by estimating the pH in urban aerosols. While current models underestimate the sulfate formation in aerosols, results in this study significantly reduced the difference between observed and modeled in both sulfates concentrations and oxygen isotopes. However uncertainties remain but it has been identified that O2+TMI oxidation pathway is dominant when pH < 5. Another oxidation pathways on alkaline dust has also been hypothetized (very speculative) to explain the high Δ 17O-values.

Response: We thank the reviewer for the valuable comments. All of them have been implemented in the revised manuscript. Please see our itemized response below.

Comments: 1. Input of stratospheric sulfates and sulfates resulting from Criegee radicals oxidation pathway are nowadays largely discussed when taking into account the S-isotopes. It is suggested that those processes are responsible for high Δ 33S-values which cannot be explained yet by current knowledge. How would those processes affect the results? Is it possible to determine their contribution? I suggest these processes being discussed.

Response: Thanks for pointing this out. Based on the theoretical mechanism of sulfate production from the gas-phase oxidation of SO_2 by stabilized Criegee Intermediats (sCI) described in Taatjes et al. (2014), the $\Delta^{17}O$ value of sulfate formed through this mechanism will be equal to 0 permil as it is the central oxygen atom of ozone is transferred to the sulfate product. Additionally, it is expected that sCIs are not important for sulfate formation in wintertime in Beijing (Pierce et al., 2013). We have reiterated in the discussion (P14L439) that all sulfate formation pathways other than ozone and H_2O_2 cannot explain the modeled low bias in $\Delta^{17}O(SO_4^{2-})$ as they produce sulfate with $\Delta^{17}O(SO_4^{2-}) = 0‰$. Given that the HPP periods occur during time periods of stable conditions and a stagnant boundary layer with little vertical mixing, the stratospheric contribution at the surface is likely minor.

Taatjes, C. A., Shallcross, D. E., and Percival, C. J.: Research frontiers in the chemistry of Criegee intermediates and tropospheric ozonolysis, Phys Chem Chem Phys, 16, 1704-1718, doi:10.1039/c3cp52842a, 2014.

Pierce, J. R., Evans, M. J., Scott, C. E., Andrea, S. D. D', Farmer, D. K., Swietlicki, E., and Spracklen, D. V.: Weak global sensitivity of cloud condensation nuclei and the aerosol indirect effect to Criegee + SO_2; chemistry, Atmos. Chem. Phys., 13, 3163-3176, doi:10.5194/acp-13-3163-2013, 2013.

Comments: 2. The std_run model can account for the seasonality observed in the aerosols. Does the implementation of the four oxidation pathways change the results? Is it more accurate? If not, what would be the drivers?

Response: Thanks for this suggestion. The importance of four heterogeneous sulfate formation for global and seasonal variation is the focus of our next paper, and is beyond the scope of the current manuscript. In the current manuscript, we focus on autumn and winter in Beijing when $PM_{2.5}$ concentrations are highest and $\Delta^{17}O(SO_4^{2-})$ observations are available at relatively high time resolution.

Comments: 3. The RHs seem to be an important factor when it comes to understand the sulfate formation. However, as described in the paper, why would the Sichuan province be the only one to exhibit the largest enhancement of sulfate formation? Many places in China might be characterized by high humidity and air stagnation?

Response: Thanks for pointing this out. We now state in the text (P10L320): "The largest enhancement in sulfate abundance after adding the in-cloud TMI pathway occurs in Sichuan basin (around 6.5 μg m^{-3}), where simulated anthropogenic Fe and Mn from coal fly ash (Figure S4) and SO_2 are high largely due to high SO_2 emissions (Zhang et al., 2009) combined with stagnant air and high relative humidity all year (Huang et al., 2014)."

Comments: 4. The model supposes a constant contribution of primary aerosols emitted by the human. However the contribution of each sources might change depending of the seasons which should also affect the O-isotopes (towards 0 ‰). Thus how would this sources variations change the results?

Response: Thanks for this comment. The importance of four heterogeneous sulfate formation for sulfate seasonal variation is the focus of our next paper, and is beyond the scope of the current manuscript.

Comments: 5. Recent studies suggested that dust particles would be responsible for pollution in China during winter, this certaintly due to photooxidation by mineral dust. Does the new models takes into account input of dust mineral from desert etc? It has also been shown that others reactions occurred on the dust particles besides NO2 and ozone (OH for example). How would it affect the O-isotopes? What would be the contribution of this oxidation pathway during the winter? Would it change the contribution value (9%)? I suggested this being discussed.

Response: Thanks for this suggestion. Run_Het does account for desert dust. We now state in the text (P13L425) "Modeled anthropogenic dust accounts for 28% of total dust in Beijing (Figure S7), and natural dust mostly originates from the Gobi Desert in southwestern Mongolia and the Badain Jaran Desert in northern China (Zhang et al., 2003; Zhang et al., 2016). The anthropogenic dust is not abundant enough to explain the difference between the results of Uno et al. (2017) and amount of sulfate production on alkaline dust required to explain the observed $\Delta^{17}O(SO_4^{2-})$." We now present the natural and anthropogenic dust distributions in China in Figure S7.

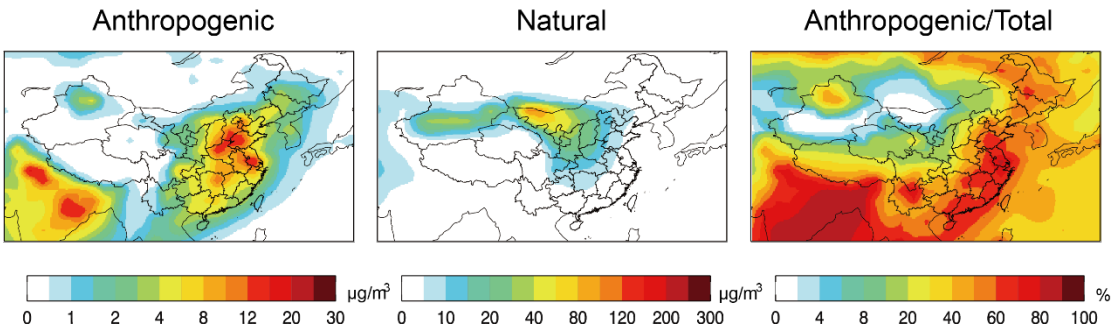

Figure S7. Modeled anthropogenic and natural dust (μg m^{-3}) at the surface, along with the percentage contribution of anthropogenic dust to total dust concentration.

Comments: 6. Although this study is very interesting and promising, results show that many uncertainties remain when it comes to understand the different oxidation pathways undertaken by SO2. I suggest that the conclusion should be more contrasted as O2+TMI cannot alone account for all the O-isotopes signatures.

Response: We agree that there are many remaining uncertainties, and that the TMI pathway is particularly uncertain due to limitations in the ability to model soluble Fe(III) and Mn(II). A discussion of this limitation is in Section Text S3. In the conclusions, we now emphasize that these results are a model prediction that is highly uncertain (P15L470): "The model predicts that TMI-catalyzed oxidation dominates heterogeneous sulfate production under calculated aerosol pH of ≤5; however, this reaction is highly uncertain due to limitations in our ability to assess modeled dissolved Fe(III) and Mn(II) concentrations."

Comments: 7. With all the pollution in China, none of the models predict high pollution in Beijing which is surprising. How could it be explained?

Response: This paper aims to investigate the potential role of different heterogeneous sulfate production mechanisms to explain this discrepancy. We have added to the introduction (P2L55) "Previous simulations have shown that most models fail to predict severe haze pollution in Beijing at least in part because of sulfate underestimation (Jiang et al., 2013; Park et al., 2014; Pozzer et al., 2012)."

Comments: 8. In Figure 1, why the SOR is not correlated to SO4 during the 11/5 ?

Response: Thanks for pointing this out. Beijing held the Asia-Pacific Economic Cooperation (APEC) Summit on 11/5-11, 2014. Stringent emission control measures were applied in Beijing and its surrounding regions to improve air quality (Zhang et al., 2016). We now state in the text P4L105 "During and before APEC, SO_2 emissions in Beijing and its surrounding regions decrease due to strict emission controls to improve air quality (Zhang et al., 2016; Liu et al., 2015b)." The increase in SOR (to ~30%) and stable sulfate concentrations during APEC likely suggest more efficient SO_2 oxidation.