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Comment on acp-2020-1279

Anonymous Referee #1

Referee comment on "Isotopic constraints on atmospheric sulfate formation pathways in the Mt. Everest region, southern Tibetan Plateau" by Kun Wang et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2020-1279-RC1>, 2021

This study presents two-season's triple oxygen isotope data for atmospheric secondary sulfate (SAS) from the Mt. Everest region or Tibet Plateau (TP), a geographic-climatically unique area. The data reveal an unexpected seasonal trend with the monsoon season having higher $\Delta^{17}\text{O-SAS}$ value than the pre-monsoon season. The data are consistent with the observed neutral to alkaline rainwater in the region, indicating an enhanced O_3 pathway in S(IV) oxidation. I have some comments on lab procedures and the explanations based on simple correlations vs. GEOS-CHEM modeling.

Three major issues:

- The laboratory procedure has a discrepancy. I could not connect the heating of solid precipitates to remove organics and the IC-column separation and precipitation of Ag_2SO_4 (See details in my specific comments below).
- Many ad hoc explanations of the observed data seem to be unnecessary if you already have an isotopically enhanced GEOS-CHEM model to account for the $\Delta^{17}\text{O-SAS}$. Of course, after the modeling results, you can highlight the major factors. But any discussion on the controlling factors should not be isolated from the modeling—which seems to me is the case in the manuscript.
- The data have NOT ruled out or considered the possibility that the SAS collected in TP was already formed in the atmosphere in South Asia. That is to say that a portion or maybe a dominant fraction of the SAS collected in the field station in TP is not formed locally but transported there in long-distance. If true, local rainwater pH should not have played a role in the elevated $\Delta^{17}\text{O-SAS}$ value. This requires the GEOS-CHEM modeling results to clarify.

Some of the specifics while I was reading over the manuscript.

Abstract: The scientific problem is not specifically expressed. Something “poorly characterized” is not a reason for research because almost everything is “poorly characterized” to an unspecified standard.

58-59: “It contains the largest land ice masses outside the poles and supplies water for more than one billion people (Immerzeel et al., 2010).” Please state the relevance of this fact to your study.

66: “a deep understanding” is vague in its meaning. Are you trying to link the secondary sulfate to the recent weakening of temperature seasonality in TP? A testable hypothesis that is related to sulfate formation pathway in TP would benefit the presentation of your research.

100-105: The need to do the SO₄ collection and isotope analysis is tenuous. “No observational studies” itself is not a good reason. What I am expecting to be shown is the link of sulfate formation pathways to specific climate, environmental, or meteorological issues in TP. For example, if indeed Indian subcontinent is supplying atmospheric pollutants to TP, what should we expect to see in the $\Delta^{17}\text{O}$ of atmospheric sulfate collected in that remote site on the northern slope of Mt. Everest? If there is an alternative source, what different $\Delta^{17}\text{O}$ -SAS are we expecting?

140-142: Before briefing on the heat treatment of “sample precipitates”, you omitted the precipitation step (e.g., did you evaporate and acidify the solution before adding BaCl₂ solution?). If this method is used, why was the method of Savarino et al (2001) and Geng et al (2013) developed specifically for smaller samples also used? If precipitates were heated at 450°C, how did you check organic matter by ion chromatography? Did you re-dissolve the precipitates? It is not mentioned in text. If the SO₄ is separated and purified by IC, why is the heating solid precipitates necessary?

Section 2.4.1: Please add the relevance of black carbon data to the SO₄ story in TP. It is not obvious to me.

Line 247-261: There is a distinct possibility that the CaSO₄ (i.e., terrigenous sulfate has a positive $\Delta^{17}\text{O}$ value) because a large portion of the sulfate in the arid surface salts could come from atmospheric deposition. Ignoring this possibility would increase the estimated $\Delta^{17}\text{O}$ of SAS, although quantitatively it is not a big deal (i.e., ~6%).

341-352: Do you really need this simple estimation of minimum and maximum O₃ path fraction involved in SAS formation? I am afraid that such a discussion does not add to the story. I thought you have already run modeling that incorporates meteorological data and atmospheric chemistry (isotope-enabled) and transport, i.e., GEOS-CHEM. The model should give you more accurate prediction of the respective fractions of O₃ pathway during

pre-monsoon and monsoon reasons. The simple minimum and maximum estimations ignore other pathways such as Mn-Fe catalyzed cloud-water O₂ oxidation and mineral-surface heterogeneous oxidation.

359: Please change "SR" to "solar radiation" because you only used the abbreviation twice (another in line 216) in the entire paper.

360: Change "hypothesize" to "explain".

363: Change "hypothesis" to "explanation".

375-381: Now, my understanding here is that the GEOS-CHEM atmospheric chemistry-transport model (isotopically enabled) could not offer a prediction on the SAS $\Delta^{17}\text{O}$ value for the pre-monsoon and monsoon reasons. Correct? If true, what's the point of doing the modeling?

398-406: There could be no major problem with an acidic cloud-water in these cited models. The problem could be the poor parametrization of heterogeneous oxidation of SO₂ or aqueous S(IV) on dust surface.

Section 3.3.4.: Your explanation of the higher $\Delta^{17}\text{O}$ during monsoon season is due to the enhanced moisture on alkaline dust surface which increases the overall fraction of the S(IV) + O₃ reaction pathway than during the pre-monsoon when the air is relatively drier. If so, it is worth of another repeat here. Please also link and explain the opposite trends in the $\Delta^{17}\text{O}$ between NO₃⁻ and SO₄ in this framework (it can be explained).

Importantly, if none of these surface heterogeneous reaction, nature and flux of dust particles, or the enhancing effect of moisture was incorporated in the GEOS-CHEM model, I wonder why you need to do the GEOS-CHEM modeling at all. On the other hand, if the model can do the job in explaining the observed $\Delta^{17}\text{O}$ data, why would you need to single out some of the factors and do the simple minimum/maximum estimates and interpretation? That is something that confuses me.

Summary: I think the $\Delta^{17}\text{O}$ -SO₄ data are solid, unique, interesting, and can be explained by known reaction mechanisms. With proper cleaning-up and reorganization of the flow of the manuscript, the data may reveal important unknown parameters we need to calibrate

and therefore quantitatively improve the isotope prediction of the GEOS-CHEM model.