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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Seasonality in the Δ^{33}S measured in urban aerosols highlights an additional oxidation pathway for atmospheric SO_2" *by* D. Au Yang et al.

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General Comments:

The number of reports on modern atmospheric sulfate with non-mass-dependently (NMD) anomalous 33S and/or 36S has been increasing in the last few years. The occurrence of these NMD sulfur isotope anomalies, with Δ33S values ranging from -0.6 to 0.5‰ in modern atmospheric sulfate is puzzling because NMD sulfur isotope signatures were initially assumed to be produced only by high-energy UV photolysis of SO2. In today's atmosphere where O2 is at 21%, only wavelength longer than ∼320 nm is available at troposphere where most SO2 emission resides. Thus, SO2

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photo-oxidation, instead of SO2 photolysis, has been proposed by some to be a likely mechanism for the observed anomalies. But experimental results do not really match with the sparse observational data. Magnetic isotope effect may play a role in generating the sulfur NMD signatures, but available data do not always have both Δ33S and Δ36S values for checking. A recent paper by Lin et al (PNAS, 2018) best summarized the current state of our knowledge and gaps on the origin and distribution of NMD S isotope anomalies seen among atmospheric sulfate including those volcano and combustion sourced.

At this state of our knowledge, more observational data are badly needed. Although not explicitly expressed or rationalized, Au Yang and his colleagues in this manuscript set out to test the hypothesis that the most positive aerosol sulfate Δ33S value should be found in remote areas far away from the city (Montreal, Canada) and there might be a seasonality change in the Δ33S value due to seasonal contribution change of local anthropogenic emission. They collected PM10 aerosol samples weekly in 2013 from 5 stations in the city of Montreal, Canada and its vicinity. Chemical and multiple S isotope compositions (δ34S, Δ33S, and Δ36S) were measured.

The results reflect some unique aspects of the Montreal PM10 sulfate. For example, the δ34S does not have good seasonality as those observed in Beijing or predicted by some model (Harris et al, 2013). The Δ33S values are largely positive, ranging from -0.08 to 0.34‰ which are similar to values for Beijing's PM10 in summer time (Guo et al., 2010) while very different from the rather negative Δ33S values for Beijing's PM2.5 sulfate in winter (Han et al., 2017). The Montreal PM10 Δ36S data have both positive and negative values and do not have a distinct seasonality.

Au Yang et al then compared their data with existing modern aerosol sulfate data with a focus on the chemical pathways of the atmospheric sulfate formation. The discussion section is very through in coverage. They also proposed their own explanations, albeit rather speculative ones.

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Overall, this manuscript offered a much-needed new set of observational data together with suggested new mechanistic interpretations on the puzzling NMD S isotope compositions in modern aerosol sulfate. Although an eventual answer is not given, the data should raise new attention to this persistent puzzle.

Specific Comments:

1. After entertaining various possible mechanisms for the observed NMD S isotope data, the authors settled one of the mechanisms (Page 17, line 4-5): "We suggest that the SO2 photooxidation reaction may occur at the dust surface and, by oxidizing the surrounding SO2 into sulfates, it would deplete the resulting SO4 in 33S and by mass balance, leave the residual SO2 enriched in 33S (Figure 6)." I suggest the authors to keep this proposal short and maybe add that such a hypothesis can be tested in the future via experiments. I think Figure 6 is probably not necessary because it has too many reaction steps and isotope fractionation signs that are themselves very uncertain. The observed sulfate Δ33S data from Antarctica snowpack (Baroni et al., 2007) show that the sulfate Δ33S may change from positive to negative over time during one eruption, suggesting that the SO2 to SO4 conversion step may be associated with a 33S enrichment (Δ33S being positive initially) in product SO4; and it is the leftover SO2 being NMD depleted in 33S which will later turn into SO4. If true, this "elementary" SO2 to SO4 photo-oxidation step in volcanic plumes would have the opposite sign in 33S anomaly to that from tropospheric SO2 oxidation to SO4 as the author proposed. I suggest this difference be discussed.

2. Page 18 line 9-11: Please note that Han et al (2017)'s sulfate were from PM2.5 while Guo et al. (2010) from PM10. The Δ33S values for Han et al are distinctly negative in winter months while for Guo et al's larger particles are distinctly positive in the months of March to August. Therefore, this pattern is not consistent with the authors' prediction of more negative-Δ33S sulfate being preferentially found in larger dust particles. I suggest incorporating this difference in your discussion as well.

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Technical corrections:

Page3 line 3-8: β value in stable isotope community has been reserved for a fundamental concept, i.e. the equilibrium fractionation factor between a compound and its atomic form of element of interest, e.g., the equilibrium fractionation factor between CO2 and O for oxygen isotopes or SO4 and S for sulfur isotopes (Richet et al., 1977). Most in the triple-isotope community use the Greek symbol θ to describe the triple sulfur or triple oxygen isotope relationship, such as 33θ and 17θ., to avoid confusion. If you insist using β, please mention θ.

Page3 Line 7 and 11: If the "deviation" at Line 7 refers only to temperature effect, then Line 11 is ok. Otherwise, Line 11's "Non-zero" cases include the deviation mentioned at Line 7. Therefore, either add the term "temperature" at Line 7 or delete "also" at Line 11.

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