

Interactive comment on “Seasonality in the $\Delta^{33}\text{S}$ measured in urban aerosols highlights an additional oxidation pathway for atmospheric SO_2 ” by D. Au Yang et al.

Anonymous Referee #2

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It has been a long question regarding the origin(s) of the non-zero capital delta S-33 and S-36 values observed in tropospheric aerosols. Although earlier studies suggested the potential transfer of stratospheric aerosol could be the source, unknown tropospheric sources or mechanisms can't be ignored. Yang et al reported new capital delta S-33 and S-36 values of sulfate aerosols observed year-round in Montreal, the values show some common features as observed in other locations except for the very low D33S values observed in Beijing. The authors thoughtfully discussed potential sources contributing to the observed non-zero capital delta S-33 and S-36 values, and suggested oxidations by Criegee intermediates and/or photo-oxidation of SO_2 on the surface of mineral dust could be responsible for the observations. Although the conclu-

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sion is rather speculative, it again calls attentions to the unusual non-zero capital delta S-33 and S-36 values observed frequently in the troposphere, which can neither explained by conventional photo-chemical theme nor well-known oxidation mechanisms.

The proposed photo-oxidation in the presence of mineral dust is inspiring. However, I don't think sulfate with direct or indirect interactions with long-range transported mineral dust would explain the observed D33S patterns, due to the probably small magnitude of this sulfate versus regional or locally produced. The residual SO₂ associated with far-away dust source region (from long range transport rooted in Asia or Sahara) maybe just too small to make any difference in D33S measured in Montreal, where local emission of SO₂ and the subsequent conversion to sulfate dominate sulfate budget.

In fact, I am confusing by the term of "Photooxidation of SO₂ in the presence of mineral dust". as based on the statements in 4.3.4., by Photooxidation of SO₂ in the presence of mineral dust, the authors seemed to mean in fact heterogenous SO₂ oxidation on the surface of mineral dust or dust enhanced HO_x radicals oxidation. If this is the case, then the term of photo-oxidation should be avoided. what's more, if this is the case, the oxidation then should be no difference from that in gaseous and aqueous phase oxidation in terms of the specific oxidation pathways (or oxidant involved), then why large non-zero D33S could be induced?

If it is really photo-oxidation of SO₂ that occurs, I don't understand why photo-oxidation only could occur on the surface of mineral dust. If mineral dust serves as the reaction site promoting the photo-oxidation of SO₂, why not other aerosols? There are studies indicating the photolysis rate of nitrate on aerosols a few orders of magnitude larger than that in the gas phase, could be this the case of SO₂? What's more, lab experiments, model calculations and ice-core data indicated when photooxidation occurs, the formed sulfate is in general enriched in S-33 and the residual SO₂ is depleted in S-33, why in this case assuming the opposite pattern? Or just to fulfill the observation?

My last comments are about the difference between the Beijing and Montreal samples.

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There are few things might be important but the authors seemed to not pay enough attentions. 1. The different SO₂ source in the two cities, especially in winter, heating source should be the main source of SO₂ but what is the difference of the energy structure between the two cities? 2. The aerosols being collected and measured, one is PM_{2.5} (the fine mode) and the other is PM₁₀ (the coarse mode). The high Na⁺ concentration in Montreal also indicate the difference, as sea-salt aerosols are often in the coarse mode. Would be sulfate formed in or associated with coarse mode aerosols isotopically different with that in fine mode? It could be another way around, as photo-oxidation of SO₂ with coarse mode aerosols leads to sulfate enriched in S-33, leaving residual SO₂ depleted in S-33 and which is ultimately converted to sulfate by heterogenous reaction in fine mode aerosols or by gaseous oxidation and then nucleate to or scavenged by fine mode aerosols. Just brainstorming as no concrete answer based on current knowledge available.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-1091>, 2018.

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