

***Interactive comment on* “Seasonality in the  $\Delta^{33}\text{S}$  measured in urban aerosols highlights an additional oxidation pathway for atmospheric  $\text{SO}_2$ ” by D. Au Yang et al.**

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Answer to review for MS acp-2018-1091

Au Yang et al., Seasonality in the  $\Delta^{33}\text{S}$  measured in urban aerosols highlights an additional oxidation pathway for atmospheric  $\text{SO}_2$  <https://doi.org/10.5194/acp-2018-1091>

We thank the two referees and Dr. Whitehill for evaluating our manuscript and providing us with feedbacks on its scientific content. The reviewers did not express any significant rebuttals, agreeing in particular with our proposition that the  $\Delta^{33}\text{S}$ -anomalies are transported to rather than produced downtown of the city. Most of the

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comments/suggestions were made to clarify/precise the SO<sub>2</sub> photooxidation process in presence of mineral dust: we included their comments, which, we believe, greatly improve the clarity of our manuscript. In particular:

- We modified section 4.4.4 Photo-oxidation where 1) we added a discussion on the distinct isotope behavior between SO<sub>2</sub> oxidation on mineral dust (our model) and in the stratosphere, as recorded in the Antarctica snowpack 2) We modified the discussion when comparing  $\Delta^{33}\text{S}$  signal between Montréal and Beijing (taking into account the different in energy sources present in both cities) and discuss differences between PM<sub>2.5</sub> and PM<sub>10</sub>, which was not present in the original version of our manuscript.

- We added a discussion in section 4.1 “Anthropogenic emissions,  $\Delta^{33}\text{S}$ -values and seasonality” the origin of the SO<sub>2</sub> and whether emitted SO<sub>2</sub> could have non-zero  $\Delta^{33}\text{S}$  due to the source-material having non-zero  $\Delta^{33}\text{S}$ ” following the point expressed by Dr. Whitehill and R#2. Reviewers’ comments appear below in blue; our detailed answers are in black and related modifications in the manuscript are reported in italics.

Referee #1: Dr. Huiming Bao

General 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 SO<sub>2</sub> photooxidation reaction may occur at the dust surface and, by oxidizing the surrounding SO<sub>2</sub> into sulfates, it would deplete the resulting SO<sub>4</sub> in <sup>33</sup>S and by mass balance, leave the residual SO<sub>2</sub> enriched in <sup>33</sup>S (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.

We agree with the reviewer’s point, that this hypothesis may not be the sole explanation to the positive and negative  $\Delta^{33}\text{S}$ -values measured in aerosols. This hypothesis, as it is described, remains speculative and could be one of the many others oxidation pathways to consider. We find no objection to keep the text concise, but still need to explain/strengthen our point and develop possible ways to test our model (R#2 was

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confused with our wording/explanation). We have clarified the text accordingly I.4 p.18.

I think Figure 6 is probably not necessary because it has too many reaction steps and isotope fractionation signs that are themselves very uncertain.

We understand the reviewer's point. However, we believe that Figure 6 is useful for the reader as it is meant to clarify our view and feel that it should be kept as is. Still, given that these reactions are described in the text, we simplified to our best Figure 6 in the new version of the manuscript. The observed sulfate  $\Delta^{33}\text{S}$  data from Antarctica snowpack (Baroni et al., 2007) show that the sulfate  $\Delta^{33}\text{S}$  may change from positive to negative over time during one eruption, suggesting that the  $\text{SO}_2$  to  $\text{SO}_4$  conversion step may be associated with a  $^{33}\text{S}$  enrichment ( $\Delta^{33}\text{S}$  being positive initially) in product  $\text{SO}_4$ ; and it is the leftover  $\text{SO}_2$  being NMD depleted in  $^{33}\text{S}$  which will later turn into  $\text{SO}_4$ . If true, this "elementary"  $\text{SO}_2$  to  $\text{SO}_4$  photo-oxidation step in volcanic plumes would have the opposite sign in  $^{33}\text{S}$  anomaly to that from tropospheric  $\text{SO}_2$  oxidation to  $\text{SO}_4$  as the author proposed. I suggest this difference be discussed.

This is a good point that was worth being mentioned, a point also highlighted by R#2 (see below). → A section I.20 p.18 was added: "It is worth mentioning that our model would thus generate a different temporal pattern from the one recorded in sulfates from the Antarctica snowpack which are first characterized by positive  $\Delta^{33}\text{S}$ -values that then shift to negative  $\Delta^{33}\text{S}$ -values, reflecting a depletion in  $^{33}\text{S}$  in the residual  $\text{SO}_2$  pool (Baroni et al., 2008;Gautier et al., 2018). Although the origin of the  $\Delta^{33}\text{S}$ -values in snowpack remains unclear, a combination of different oxidation pathways with similar contributions of S-MDF (high or lower contribution of OH oxidation pathway) and S-MIF processes (photoexcitation and photolysis) has been recently suggested to explain such  $\Delta^{33}\text{S}$ -values (Gautier et al., 2018). The OH oxidation pathway is occurring in both the troposphere and the stratosphere. However, in the troposphere as i) photolysis cannot occur because of the ozone layer and ii) photooxidation would only occur in a narrow range of UV (see section 4.4.2.) but would unlikely display a seasonal variation, we suggest that the reactions responsible for S-MIF in the stratosphere and in the

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troposphere are different. Thus, the contrasting patterns observed in sulfates in Antarctica and in Montreal could be explained by the implication of different combinations of oxidation pathways where a S-MIF process other than photolysis and photooxidation is involved.“

2. Page 18 line 9-11: Please note that Han et al (2017)'s sulfate were from PM<sub>2.5</sub> while Guo et al. (2010) from PM<sub>10</sub>. The  $\Delta^{33}\text{S}$  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- $\Delta^{33}\text{S}$  sulfate being preferentially found in larger dust particles. I suggest incorporating this difference in your discussion as well.

We agree with the reviewer that including the study of Guo et al. and highlighting the difference in aerosols sizes between Guo et al and Han et al. (PM<sub>10</sub> versus PM<sub>2.5</sub>) in the discussion is useful. Guo et al.' was not discussed in our original manuscript as the authors did not report chemical analysis for their aerosols, making it impossible to determine whether the PM<sub>10</sub> could record or be characterized by a higher contribution of dust than PM<sub>2.5</sub>. This is now discussed in the revised version of the manuscript. → A section l.33 p.19 was added: “Negative  $\Delta^{33}\text{S}$  values have also not been measured in PM<sub>10</sub> during spring. Guo et al. (2010) data show positive  $\Delta^{33}\text{S}$ -values, similar to ours and to other studies but different from Han et al. (2017). However, Guo et al. (2010) did not report major elements in their aerosol samples, making it difficult to detect any significant dust contribution. Nevertheless while Guo et al. (2010) measured sulfates S isotope compositions until April 11th, Cao et al. (2014) reported a significant dust event on April 27th of the same year. In that respect this does not contradict our hypothesis: SO<sub>2</sub> photooxidation on mineral dust could lead to positive  $\Delta^{33}\text{S}$  of the residual SO<sub>2</sub> transported to Beijing. Moreover, for our model to be consistent with the data of Han et al. (2017), their aerosol fine fraction would need to be dominated by dust which is consistent with the observation that Asian dust storms contribute to the PM<sub>2.5</sub> budget in Beijing (Han et al., 2015).”

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Technical corrections: Page3 line 3-8:  $\beta$  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 CO<sub>2</sub> and O for oxygen isotopes or SO<sub>4</sub> and S for sulfur isotopes (Richet et al., 1977). Most in the triple-isotope community use the Greek symbol  $\theta$  to describe the triple sulfur or triple oxygen isotope relationship, such as 33 $\theta$  and 17 $\theta$ ., to avoid confusion. If you insist using  $\beta$ , please mention  $\theta$ .

This is not exactly true:  $\beta$ -factor is indeed used to express the reduced partition function of molecules from which equilibrium fractionation factors are calculated. However,  $\beta$ -values are also used to express mass laws between two isotopic systems in general (e.g. Young and Galy, 2004;) while  $\theta$ - is specifically used when it corresponds to isotope equilibrium (e.g. Farquhar and Wing, 2003; Dauphas and Schauble, 2016),  $\theta$  is used to define the slope defined by data which, owing to mass conservation effects, does not necessarily correspond to  $\beta$ - (i.e. the mass exponent relating the two isotope fractionation factors (Farquhar and Wing, 2003, Ono et al., 2006; Johnston et al., 2008). Given the remaining lack of understanding on the reactions involved and the mechanisms (equilibrium, kinetic, etc. . .), we feel that we cannot use the  $\theta$ -notation. Using  $\beta$ - is, we think, therefore more appropriate. We have added some clarifications to help the reader with the 'isotope notations' which, we agree, can easily be confusing. → We modified l.5, p3: “ The  $\beta$ -exponent is usually expressed as  $\beta$  to refer to isotope equilibrium. We are using  $\beta$ - instead as the processes describing the SO<sub>2</sub>-oxidation are actually not at the isotope equilibrium. Its value depends on the reaction considered (Farquhar et al., 2001; Harris et al., 2013; Ono et al., 2013; Watanabe et al., 2009). At high temperature (> 500°C, i.e. under equilibrium), 33 $\beta$  and 36 $\beta$ -values are respectively 0.515 and 1.889 (Eldridge et al., 2016; Otake et al., 2008)”

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

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11. → This has been modified in the text.

Anonymous Referee #2 I don't think sulfate with direct or indirect interactions with long-range transported mineral dust would explain the observed  $\Delta^{33}\text{S}$  patterns, due to the probably small magnitude of this sulfate versus regional or locally produced. The residual  $\text{SO}_2$  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  $\Delta^{33}\text{S}$  measured in Montreal, where local emission of  $\text{SO}_2$  and the subsequent conversion to sulfate dominate sulfate budget.

This is a good point raised by the reviewer. However it would be possible to account for the  $\Delta^{33}\text{S}$ -values with a small contribution of this oxidation pathway. If 1) the sulfates formed by photooxidation on mineral dust were characterized by high  $\Delta^{33}\text{S}$ -values (hypothetically 10‰, and 2) would hypothetically contribute to  $\sim 10\%$  of the total sulfate, then even a small contribution of those sulfates, mixed with sulfates formed by the major oxidation pathways, which are locally produced (i.e.  $\Delta^{33}\text{S} \sim 0\%$ , could explain the  $\Delta^{33}\text{S}$  -values observed in the troposphere ( $\Delta^{33}\text{S} < 0.5$ ). → We have made this point clearer I.15 p.19 : “If this latest oxidation pathway could promote the formation of sulfates characterized by high  $\Delta^{33}\text{S}$ -values (hypothetically 10‰, then a small contribution (hypothetically  $\sim 10\%$ ) from this oxidation pathway would produce a significant signal on the sulfur isotope composition of tropospheric sulfate aerosols (i.e.  $\Delta^{33}\text{S} \sim 1\%$  based on these hypotheses). In this case, even a small proportion of those sulfates mixed with sulfates formed by the major oxidation pathways locally produced (i.e.  $\Delta^{33}\text{S} \sim 0\%$  could explain the  $\Delta^{33}\text{S}$ -values observed in the troposphere ( $\Delta^{33}\text{S} < 0.5\%$ . This hypothesis needs to be further tested.”

In fact, I am confusing by the term of “Photooxidation of  $\text{SO}_2$  in the presence of mineral dust”. as based on the statements in 4.3.4., by Photooxidation of  $\text{SO}_2$  in the presence of mineral dust, the authors seemed to mean in fact heterogenous  $\text{SO}_2$  oxidation on the surface of mineral dust or dust enhanced  $\text{HO}_x$  radicals oxidation. If this is the case, then the term of photo-oxidation should be avoided. Our use of ‘photooxidation’

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is actually meant to be consistent with the literature reporting “photooxidation of SO<sub>2</sub> on mineral dust” (Yu et al., 2017; He et al., 2014; Dupart et al., 2012; George et al., 2015; Usher et al., 2003; Zhao et al., 2018; Ma et al., 2018).

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 D<sub>33S</sub> could be induced? We agree about the specific mechanism (SO<sub>2</sub> oxidation by OH) but little is known about the number of other mechanisms behind ‘the in-particle chemistry’; heterogeneous SO<sub>2</sub> oxidation by OH radicals have been described (as mentioned by R#2) but oxidation by other radicals may exist, such as the recently identified superoxide O<sub>2</sub><sup>-</sup>. The S-isotope fractionations associated with this latest oxidation pathway have not been reported yet. Furthermore, others radicals/oxidants might as well be discovered in the future, leading SO<sub>2</sub> oxidation by mineral dust to produce specific S-isotope fractionation factors compared to OH-oxidation. → We included R#2’s comment and have clarified our point accordingly: “To date, the mechanisms behind the in-particle chemistry remain little studied and several SO<sub>2</sub> heterogeneous oxidation reactions may have been overlooked” l.7 p.16. We also changed the text as follows: “The oxidation implicating heterogeneous oxidation and OH radicals should a priori not show significant differences from the one that occurs in gaseous and aqueous phase; i.e. heterogeneous oxidation of SO<sub>2</sub> is likely to induce a mass dependent fractionation of S-isotopes (Harris et al., 2012) with resulting negative  $\Delta^{33}\text{S}$ -values  $< -0.15\text{‰}$  (Harris et al., 2013). Among other reactions, SO<sub>2</sub> oxidation by the O<sub>2</sub><sup>-</sup> superoxide radical anion is another oxidation reaction that has not yet been isotopically characterized (Dupart et al., 2014; Usher et al., 2003). If this latest oxidation pathway could promote the formation of sulfates characterized by high  $\Delta^{33}\text{S}$ -values (hypothetically 10‰, then a small contribution (hypothetically ~10%) from this oxidation pathway would produce a significant signal on the sulfur isotope composition of tropospheric sulfate aerosols (i.e.  $\Delta^{33}\text{S} \sim 1\text{‰}$  based on these hypotheses). In this case, even a small proportion of those sulfates mixed with sulfates formed by the major oxidation pathways locally produced (i.e.  $\Delta^{33}\text{S} \sim$

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0‰ could explain the  $\Delta^{33}\text{S}$ -values observed in the troposphere ( $\Delta^{33}\text{S} < 0.5\text{‰}$ ). This hypothesis needs to be further tested “ I.10 p.19

If it is really photo-oxidation of  $\text{SO}_2$  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  $\text{SO}_2$ , why not other aerosols? It may well be but, to our knowledge, no study has ever reported photooxidation of  $\text{SO}_2$  in the presence of other types of C-rich, i.e. 'organic,' aerosols. This could result from the low concentration of metal oxides in other aerosols (Cass et al., 2000).

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  $\text{SO}_2$  ? Compared to nitrate, photolysis of the sulfate is less likely because the main wavelength region of  $\text{SO}_2$ -absorption (190-220 nm) is filtered by the ozone layer. However, as stated in section 4.3.2, a narrow wavelength range (typically 320 to 330 nm) where  $\text{SO}_2$  absorption could occur (i.e. not filtered by the ozone layer) in the troposphere, which still leaves room for S-MIF to be produced. This is better stated in the text I.23 p.15.

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  $\text{SO}_2$  is depleted in S-33 We have addressed this point above.

Why in this case assuming the opposite pattern? Or just to fulfill the observation? Indeed, this is inferred, not observed. The text now states more clearly this aspect I.4 p18

1. The different  $\text{SO}_2$  source in the two cities, especially in winter, heating source should be the main source of  $\text{SO}_2$  but what is the difference of the energy structure between the two cities?

R#2's comment can be understood in two ways: (a) distinct oxidation processes of sulfur dioxide with  $\Delta^{33}\text{S} \sim 0 \text{‰}$  (here low vs high temperature of combustion) leading to

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markedly distinct isotope signals in Beijing aerosols and (b) distinct sulfur sources having distinct, non-zero  $\Delta^{33}\text{S}$ . Point 'b' is somewhat similar to the comment expressed below by Dr Whitehill. a- Both Montréal and Beijing have their energy relying primarily on coal and oil burning. The main difference probably lies in the temperature of combustion of coal and wood (see Han et al., 2016; Lin et al. 2018) where 'low temperature combustion' would be more significant in Beijing and considered as a possibility to account for the distinctly negative  $\Delta^{33}\text{S}$  of aerosols (Han et al., 2016; Lin et al., 2017). However, Lin et al. (2018) recently questioned this mechanism on the basis of new results (low temperature combustion would not lead to very anomalous  $\Delta^{33}\text{S}$ , yet with still significant non-zero  $\Delta^{36}\text{S}$ -values). We cannot discard this possibility but tried, using available data, to investigate whether  $\text{SO}_2$  photo-oxidation on mineral dust could represent a viable alternative hypothesis. The revised manuscript states more clearly that additional data are required to discuss such a possibility. b- As suggested by Dr Whitehill in his comment, the question could also relate to distinct sources of sulfur with different  $\Delta^{33}\text{S}$  -values. This is addressed below.

→We modified the discussion I.30 p.12: “ This contrasts with the interpretation where the negative  $\Delta^{33}\text{S}$ -values (down to  $-0.6\text{‰}$  measured during winter in Beijing would relate to anthropogenic sources, in particular those generating incomplete, i.e. low-temperature, coal or wood combustion (Han et al., 2017). Still, this model cannot explain the total range of isotope compositions observed. The authors mostly rely on data showing that primary aerosols are characterized by negative  $\Delta^{33}\text{S}$ -values but only down to  $-0.2\text{‰}$  (Lee et al., 2002). Also the complementary positive  $\Delta^{33}\text{S}$  still need to be addressed. Furthermore, Han et al. (2017) interpretation would predict: i) a seasonality with negative  $\Delta^{33}\text{S}$ -values down to  $-0.6\text{‰}$  during winter as a result from increased coal and wood burning and ii) a gradient in the  $\Delta^{33}\text{S}$ -values from the outer towards the inner city with isotope shifting from  $\sim 0\text{‰}$  to negative  $\Delta^{33}\text{S}$ -values. This would contradict our observations, since our data in Montreal show the opposite to what was observed in Beijing. It comes that based on the available data of S anthropogenic emissions, the combustion of coal or wood at low temperature can neither explain

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the  $\Delta^{33}\text{S}$  seasonality nor the highest  $\Delta^{33}\text{S}$ -values up to 0.5‰ measured in urban aerosols. This conclusion is reinforced by the fact that coal is not the major source of energy in Montreal, oil representing 50% of the fuel energy in Quebec (Montréal, 2015). Oil would thus display  $\Delta^{33}\text{S}$ -values close to 0‰ (Lee et al., 2002). Taken together, our observations suggest that anthropogenic activities (both coal and oil combustion) are unlikely responsible for the  $\Delta^{33}\text{S}$  seasonality nor the highest  $\Delta^{33}\text{S}$ -values up to 0.5‰ measured in Montreal urban aerosols. This implies that non-zero  $\Delta^{33}\text{S}$ -values are produced in rural rather than in urban environments. Thus, the following discussion mostly focuses on data from station 98, located on the western part of the island, upstream of the main blowing winds and supposedly less affected by emissions from local anthropogenic activities.”.

2. The aerosols being collected and measured, one is PM<sub>2.5</sub> (the fine mode) and the other is PM<sub>10</sub> (the coarse mode). The high Na<sup>+</sup> concentration in Montreal also indicates 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 SO<sub>2</sub> with coarse mode aerosols leads to sulfate enriched in S<sub>33</sub>, leaving residual SO<sub>2</sub> depleted in S-33 and which is ultimately converted to sulfate by heterogeneous 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.

The reviewer raises an interesting issue and we agree that S-isotopes of sulfates formed in the aerosol coarse mode could be different from the one in the fine mode fraction. To our knowledge, no study (neither experimental nor with natural samples) has ever been published yet but we fully agree that this is a prediction that can be made from our model, which we have included in the revised manuscript. Besides, the hypothesis expressed by the reviewer: “It could be another way around, as photo-oxidation of SO<sub>2</sub> with coarse mode aerosols leads to sulfate enriched in S<sub>33</sub>, leaving

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residual SO<sub>2</sub> depleted in S-33 and which is ultimately converted to sulfate by heterogeneous reaction in fine mode aerosols or by gaseous oxidation and then nucleate to or scavenged by fine mode aerosols” is also interesting. However, following this hypothesis, positive  $\Delta^{33}\text{S}$ -values would have been explained by the input of sulfates associated with dust, which is not consistent with our chemical analyses that do not indicate any contributions of mineral dust to Montreal aerosols. Moreover, in this case, we would expect negative  $\Delta^{33}\text{S}$ -values on sulfates collected at station 98 (the station least impacted by anthropogenic emissions) which is not the case. For these reasons, this hypothesis cannot account for our observations. We made this clearer in the manuscript.

→ We modified the discussion I.4 p.18 as follows: “Thus, in order to explain our data (i.e. most positive  $\Delta^{33}\text{S}$ -values at station 98, seasonality of the S-isotope compositions, no dust particles detected in Montreal aerosols), we suggest that the SO<sub>2</sub> photooxidation reaction may occur at the dust surface and, by oxidizing the surrounding SO<sub>2</sub> into sulfates, it would deplete the resulting SO<sub>4</sub> in <sup>33</sup>S and by mass balance, leave the residual SO<sub>2</sub> enriched in <sup>33</sup>S (Figure 6). Sulfates associated to dust would be characterized by negative  $\Delta^{33}\text{S}$ -values and will be deposited while the residual atmospheric SO<sub>2</sub> (i.e. characterized by positive  $\Delta^{33}\text{S}$ -values) would be transported to Montreal. The transported SO<sub>2</sub> enriched in <sup>33</sup>S would then be oxidized into sulfates in Montreal vicinity through the major oxidation pathways (O<sub>2</sub>+TMI, H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, OH, NO<sub>2</sub>). We suggest the presence of two different types of sulfates: i) the first type would be formed by photooxidation and would be associated to coarse particles (dust particles) while ii) the second type would be formed by the oxidation of the remaining SO<sub>2</sub> and thus likely be associated to finer particles. These sulfates supposedly characterized by positive  $\Delta^{33}\text{S}$  up to 0.5‰ would be mixed with both primary and secondary sulfates emitted and formed within the city and supposedly characterized by  $\Delta^{33}\text{S}$ -values close to 0‰ (i.e. oxidation by O<sub>2</sub>+TMI, H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, OH, NO<sub>2</sub> ; Figure 6). “ “

Comment #1 : Dr. Andrew Whitehill I would like to see more discussion about the

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$\Delta^{33}\text{S}$  values of the initial  $\text{SO}_2$  and more justifications / measurements / citations for these assumptions. Iron production in the Quebec / Ontario region of Canada is a high emitter of sulfur dioxide. My first order assumption would be that processing iron from Archean banded iron formations would release  $\text{SO}_2$  with non mass dependent isotope signatures.  $\text{SO}_2$  signatures from this region can be transported long distances and may contribute to non mass dependent isotope signatures significantly downwind (e.g. Boston, MA). It would be useful to understand your reasoning as to why either (1)  $\text{SO}_2$  emitted from processing iron from banded iron formations will not produce non mass dependent  $\text{SO}_2$  or (2) this is not a substantial source of  $\text{SO}_2$  for this region and will not affect the observed isotope signatures. You invoke complex reactions (e.g.  $\text{SO}_2$  photooxidation and stabilized Criegee intermediates) without constraining the  $\text{SO}_2$  source signature. A mixing of  $\text{SO}_2$  from different sources would have different  $\delta^{34}\text{S}$  (and likely  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$ ) values and may contain seasonality as observed in this study.

Below are the answers to the two questions. It would be useful to understand your reasoning as to why (2) this is not a substantial source of  $\text{SO}_2$  for this region and will not affect the observed isotope signatures

The large majority of coal and oil used worldwide for energy are derived from Proterozoic sediments (<2.3 Gy) and, as such, does not have significant non-zero  $\Delta^{33}\text{S}$  (typically within  $\pm 0.1\text{‰}$ , e.g. Farquhar and Wing, 2003). The complete conversion of sulfur (as organic S, sulfate and/or pyrite) to  $\text{SO}_2$  implies that it would have the same isotope composition than that of its starting material, i.e. no isotope fraction and  $\Delta^{33}\text{S} = 0.0 \pm 0.1\text{‰}$ . Only if part of the  $\text{SO}_2$  is scavenged and the fractionation process is strongly non-mass dependent ( $\beta \neq 0.515$ ) would the emitted  $\text{SO}_2$  have non-zero  $\Delta^{33}\text{S}$ . 'Low temperature combustion' was suggested to represent such a process. However, this is dealing with identifying processes. Dr Whithill and R#2 wonders whether the source of sulfur could be characterized by non-zero  $\Delta^{33}\text{S}$ , with an emphasis on iron mining, which relies on the extraction of some Archean banded-iron formation mining. These

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kinds of samples can have high S-content (several percent) with significant non-zero  $\Delta^{33}\text{S}$  (typically positive  $\Delta^{33}\text{S}$ -values, up to several per mille). This is a possibility that we did not originally address.

Iron production in the Quebec / Ontario region of Canada is indeed an emitter of sulfur dioxide. However, with a total of 5800 tons of  $\text{SO}_2$  emission each year (Environnement Canada, 2013), this only represents 1.5% of the total 370000 tons of  $\text{SO}_2$  emitted (Environnement Canada, 2013). It would be useful to understand your reasoning as to why (1)  $\text{SO}_2$  emitted from processing iron from banded iron formations will not produce non mass dependent  $\text{SO}_2$ . By considering that 1) the BIF are characterized by a  $\Delta^{33}\text{S}$ -values up to 2‰ (Thomassot et al., 2015), 2) iron process does not fractionate the sulfur isotopes (similar to coal combustion) and 3) only 1.5% of the  $\text{SO}_2$  results from iron processing (Environnement Canada, 2013), this would only produce  $\Delta^{33}\text{S}$ -anomalies up to 0.02‰. Thus, iron processing can hardly account for the origin of non-zero  $\Delta^{33}\text{S}$ -values observed in most aerosols. More specifically, Canadian iron ore production is split in ~50-45% between Quebec and Labrador (with 5% in Nunavut). With respect to Quebec, iron production is mainly from Algoma BIFs of about 2.8-2.7 Ga, typified by the Temagami deposit for which there are recently available  $\Delta^{33}\text{S}$  data (Diekrup et al., 2018). From their Table 1, all their sedimentary data (oxidic facies, cherts, BIF sulphides; sulphidic clays; sulphide veins) gives an average of  $0.467 \pm 0.707$  (one standard deviation;  $n=50$ ), which makes emitted  $\text{SO}_2$  having even smaller  $\Delta^{33}\text{S}$ .

→ Section 4.1 “ Anthropogenic emission,  $\Delta^{33}\text{S}$  -values and seasonality” has been modified “1.3 p.12 : “The large majority of coal and oil used worldwide as an energy source are extracted from Proterozoic sediments (<2.3 Gy) and, as such, does not have significant non-zero  $\Delta^{33}\text{S}$  (typically within  $\pm 0.1\%$  e.g. Farquhar and Wing, 2003). The complete conversion of sulfur (as organic S, sulfate and/or pyrite) to  $\text{SO}_2$  implies that  $\text{SO}_2$  has the same isotope composition than that of its starting material, i.e. no isotope fractionation or  $\Delta^{33}\text{S} = 0.0 \pm 0.1\%$ . Only if part of the  $\text{SO}_2$  is scavenged

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and the fractionation process is strongly non-mass dependent ( $\beta \neq 0.515$ ) would the emitted SO<sub>2</sub> have a non-zero  $\Delta^{33}\text{S}$ . Han et al. (2016) suggested that the combustion of coal or wood at low temperature may represent such conditions. Iron extraction from Archean banded-iron formation (BIF) is another source of atmospheric S that therefore produces non-zero  $\Delta^{33}\text{S}$ . However, the 5,800 tons of SO<sub>2</sub> emitted each year in the Quebec/Ontario region by mining activities (Environnement Canada, 2013) only represents 1.5% of the annual 370,000 tons of national SO<sub>2</sub> emissions (Environnement Canada, 2013). If we consider a high average  $\Delta^{33}\text{S}$  of 2‰ (Thomassot et al., 2015) and a proportion of 1.5% of SO<sub>2</sub> resulting from iron processing, this would lead to an average  $\Delta^{33}\text{S}$ -anomaly of the final SO<sub>2</sub> of up to 0.02‰. Thus, iron processing can hardly account for the origin of the non-zero  $\Delta^{33}\text{S}$ -values observed in most aerosols. More specifically, the Canadian iron ore production is split between Quebec (50%), Labrador (45%) and Nunavut (5%). With respect to Quebec, iron production is mainly operated from the Algoma BIFs (~2.8 Ga) typified by the Temagami deposits for which Diekrup et al. (2018) give an average  $\Delta^{33}\text{S}$  of  $0.467 \pm 0.707$  (samples including oxidic facies, cherts, BIF sulphides and sulphidic clays, sulphide veins), which makes the emitted SO<sub>2</sub> having even smaller  $\Delta^{33}\text{S}$ . In the following discussion we will therefore consider that sources of SO<sub>2</sub> have  $\Delta^{33}\text{S} \sim 0$ ‰ and that only specific chemical reactions (photochemical or not) can produce non-zero  $\Delta^{33}\text{S}$ .

## Reference

Boulet, D., and S. Melançon (2016), Bilan environnemental. Qualité de l'air à Montréal, Rapport Annuel 2016. Ville de Montréal, Service de l'environnement Division de la planification et du suivi environnemental, RSQA, 12.

Lee, C. W., J. Savarino, H. Cachier, and M. Thiemens (2002), Sulfur (<sup>32</sup>S, <sup>33</sup>S, <sup>34</sup>S, <sup>36</sup>S) and oxygen (<sup>16</sup>O, <sup>17</sup>O, <sup>18</sup>O) isotopic ratios of primary sulfate produced from combustion processes, *Tellus B*, 54(3), 193-200.

Lin, M., X. Zhang, M. Li, Y. Xu, Z. Zhang, J. Tao, B. Su, L. Liu, Y. Shen, and M. H. Thiemens (2018), Five-S-isotope evidence of two distinct mass-independent sulfur isotope effects and implications for the modern and Archean atmospheres, *Pro-*

[Printer-friendly version](#)[Discussion paper](#)

ceedings of the National Academy of Sciences, 115(34), 8541-8546. Thomassot, E., J. O'Neil, D. Francis, P. Cartigny, and B. A. Wing (2015), Atmospheric record in the Hadean Eon from multiple sulfur isotope measurements in Nuvvuagittuq Greenstone Belt (Nunavik, Quebec), Proceedings of the National Academy of Sciences, 112(3), 707-712. Baroni, M., Savarino, J., Cole-Årdai, J., Rai, V. K., and Thiemens, M. H.: Anomalous sulfur isotope compositions of volcanic sulfate over the last millennium in Antarctic ice cores, Journal of Geophysical Research: Atmospheres, 113, 2008. Cass, G. R., Hughes, L. A., Bhawe, P., Kleeman, M. J., Allen, J. O., and Salmon, L. G.: The chemical composition of atmospheric ultrafine particles, Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, 358, 2581-2592, 2000. Diekrup, D., Hannington, M. D., Strauss, H., and Ginley, S. J.: Decoupling of Neoproterozoic sulfur sources recorded in Algoma-type banded iron formation, Earth and Planetary Science Letters, 489, 1-7, 2018. Dupart, Y., King, S. M., Nekat, B., Nowak, A., Wiedensohler, A., Herrmann, H., David, G., Thomas, B., Miffre, A., and Rairoux, P.: Mineral dust photochemistry induces nucleation events in the presence of SO<sub>2</sub>, Proceedings of the National Academy of Sciences, 109, 20842-20847, 2012. Dupart, Y., Fine, L., D'Anna, B., and George, C.: Heterogeneous uptake of NO<sub>2</sub> on Arizona Test Dust under UV-A irradiation: An aerosol flow tube study, Aeolian Research, 15, 45-51, 2014. Eldridge, D., Guo, W., and Farquhar, J.: Theoretical estimates of equilibrium sulfur isotope effects in aqueous sulfur systems: Highlighting the role of isomers in the sulfite and sulfoxylate systems, Geochimica et Cosmochimica Acta, 195, 171-200, 2016. Environnement Canada: National Pollutant Release Inventory, 2013. Farquhar, J., Savarino, J., Airieau, S., and Thiemens, M. H.: Observation of wavelength-sensitive mass-independent sulfur isotope effects during SO<sub>2</sub> photolysis: Implications for the early atmosphere, Journal of Geophysical Research: Planets (1991–2012), 106, 32829-32839, 2001. Gautier, E., Savarino, J., Erbland, J., and Farquhar, J.: SO<sub>2</sub> oxidation kinetics leave a consistent isotopic imprint on volcanic ice core sulfate, Journal of Geophysical Research: Atmospheres, 2018. George, C., Ammann, M., D'Anna, B., Donaldson, D., and Nizkorodov, S. A.: Heterogeneous photochem-

[Printer-friendly version](#)[Discussion paper](#)

istry in the atmosphere, *Chemical reviews*, 115, 4218-4258, 2015. Han, L., Cheng, S., Zhuang, G., Ning, H., Wang, H., Wei, W., and Zhao, X.: The changes and long-range transport of PM<sub>2.5</sub> in Beijing in the past decade, *Atmospheric Environment*, 110, 186-195, 2015. Han, X., Guo, Q., Strauss, H., Liu, C.-Q., Hu, J., Guo, Z., Wei, R., Peters, M., Tian, L., and Kong, J.: Multiple sulfur isotope constraints on sources and formation processes of sulfate in Beijing PM<sub>2.5</sub> aerosol, *Environmental Science & Technology*, 2017. Harris, E., Sinha, B., Foley, S., Crowley, J., Borrmann, S., and Hoppe, P.: Sulfur isotope fractionation during heterogeneous oxidation of SO<sub>2</sub> on mineral dust, *Atmospheric Chemistry and Physics*, 12, 4867-4884, 2012. Harris, E., Sinha, B., Hoppe, P., and Ono, S.: High-precision measurements of <sup>33</sup>S and <sup>34</sup>S fractionation during SO<sub>2</sub> oxidation reveal causes of seasonality in SO<sub>2</sub> and sulfate isotopic composition, *Environmental science & technology*, 47, 12174-12183, 2013. He, H., Wang, Y., Ma, Q., Ma, J., Chu, B., Ji, D., Tang, G., Liu, C., Zhang, H., and Hao, J.: Mineral dust and NO<sub>x</sub> promote the conversion of SO<sub>2</sub> to sulfate in heavy pollution days, *Scientific reports*, 4, 2014. Lee, C. W., Savarino, J., Cachier, H., and Thiemens, M.: Sulfur (<sup>32</sup>S, <sup>33</sup>S, <sup>34</sup>S, <sup>36</sup>S) and oxygen (<sup>16</sup>O, <sup>17</sup>O, <sup>18</sup>O) isotopic ratios of primary sulfate produced from combustion processes, *Tellus B*, 54, 193-200, 2002. Ma, J., Chu, B., Liu, J., Liu, Y., Zhang, H., and He, H.: NO<sub>x</sub> promotion of SO<sub>2</sub> conversion to sulfate: An important mechanism for the occurrence of heavy haze during winter in Beijing, *Environmental Pollution*, 233, 662-669, 2018. Montréal, V. d.: Reduced dependence on fossil fuels in Montréal 2015. Ono, S., Whitehill, A., and Lyons, J.: Contribution of isotopologue self-shielding to sulfur mass-independent fractionation during sulfur dioxide photolysis, *Journal of Geophysical Research: Atmospheres*, 118, 2444-2454, 2013. Otake, T., Lasaga, A. C., and Ohmoto, H.: Ab initio calculations for equilibrium fractionations in multiple sulfur isotope systems, *Chemical Geology*, 249, 357-376, 2008. Thomasot, E., O'Neil, J., Francis, D., Cartigny, P., and Wing, B. A.: Atmospheric record in the Hadean Eon from multiple sulfur isotope measurements in Nuvvuagittuq Greenstone Belt (Nunavik, Quebec), *Proceedings of the National Academy of Sciences*, 112, 707-712, 2015. Usher, C. R., Michel, A. E., and Grassian, V. H.: Reactions on min-

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eral dust, *Chemical Reviews*, 103, 4883-4940, 2003. Watanabe, Y., Farquhar, J., and Ohmoto, H.: Anomalous fractionations of sulfur isotopes during thermochemical sulfate reduction, *Science*, 324, 370-373, 2009. Yu, Z., Jang, M., and Park, J.: Modeling atmospheric mineral aerosol chemistry to predict heterogeneous photooxidation of SO<sub>2</sub>, *Atmospheric Chemistry and Physics*, 17, 10001-10017, 2017. Zhao, D., Song, X., Zhu, T., Zhang, Z., Liu, Y., and Shang, J.: Multiphase oxidation of SO<sub>2</sub> by NO<sub>2</sub> on CaCO<sub>3</sub> particles, *Atmospheric Chemistry and Physics*, 18, 2481-2493, 2018.

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