

Interactive comment on “Oxygen and sulfur mass-independent isotopic signatures in black crusts: the complementary negative $\Delta^{33}\text{S}$ -reservoir of sulfate aerosols?” by Isabelle Genot et al.

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First of all, there was no rebuttal to our interpretations and the comments raised by the second referee were important to improved our manuscript. We almost followed all of them.

1) "The manuscript is too long and there is too much information. I think the most important finding of this manuscript is the observation of negative D33S values. I believe that the authors agree with me as they also put this information in the title. However,

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the authors used 5-6 pages to discuss d18O, d34S, and D17O data, which may be distracting. I agree that some discussions in those parts are important to support the authors' interpretation, but in my point of view, many of them may be unnecessary and even irrelevant (e.g., lines 370-375). I understand that everyone has his/her own writing style, but I am afraid that some readers will get lost in this manuscript. My suggestion is that the authors should shorten the d18O, d34S, and D17O discussions, and highlight their most important findings (i.e., the negative D33S data). Though I will leave it for the authors to decide as to whether they prefer keeping their writing style."

We think that before arguing that the origin of the $\Delta^{33}\text{S}$ anomaly lies in a "process" rather than a "source", it is a pre-requisite to address if S and O isotopic compositions are affected by processes (e.g. SO₂ partial oxidation, gypsum precipitation...) even if it only slightly overprints the source signatures. It would otherwise confuse the reader having two sections, one dealing with mixing (d34S-d18O- $\Delta^{17}\text{O}$), the other dealing with processes (d34S- $\Delta^{33}\text{S}$ - $\Delta^{36}\text{S}$). We added our developed reasoning L247-251. Given that d34S-d18O variation is explained by a mixing, representing source signatures and that $\Delta^{17}\text{O}$ -values are evidence for atmospheric aerosols, we know that $\Delta^{33}\text{S}$ signature is not overprinted and that the source or process leading to this anomaly is atmospheric (not coming from the host-rock). We merged d34S-18O- $\Delta^{17}\text{O}$ sections, keeping the discussion about processes even if mixing is the main mechanism and reduced the text by ~ 1.5 pages for this part of the discussion, almost 20% of the 50% asked by the first referee. Furthermore, we added details asked by both referees which does not allow us to reduce the text as much. The discussion is very detailed and as the referee said, it is the writing style of our laboratory because we think that most of the time, the interpretation is limited to a mixing without discussing other processes. Furthermore, various scientific communities could be interested in this paper without understanding all concepts covered (e.g. black crusts, stable isotope geochemistry in the atmosphere, mass-independent fractionation). Consequently, we wish to keep a detailed, rigorous and accordingly developed discussion to allow everyone a good comprehension.

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2) "In the introduction, the current state and gap of our knowledge on S-MIF (especially D33S) is not well presented. It is true that most aerosol measurements displayed positive D33S values, but negative D33S values were also noted by previous works by Lee et al. (2002), Shaheen et al. (2014), Han et al. (2017), and Lin et al. (2018a). In addition, I suggested the authors highlighted their recent work (Au Yang et al., 2019) in the introduction. Au Yang et al., (2019) suspected that photooxidation of SO₂ on the surface of mineral dusts may produce large S-MIF signatures, and the gypsum layer on carbonate studied in this study is a natural laboratory to test their hypothesis and concept model."

We agree and referred to previous works (L61-76) reporting negative $\Delta^{33}\text{S}$ -values. As suggested by the referee, we also highlighted the study of Au Yang et al., (2019) which proposes a model to counterbalance $\Delta^{33}\text{S} > 0\text{‰}$ in sulfate aerosols.

3) "The authors listed some end-members to quantify the anthropogenic contribution, but it is not clear how the authors defined their isotopic values. For example, in line 289, it was mentioned that the end-member CAS/PL has a D17O value of zero per mil. Did the author measure the CAS/PL? Is this value just a simple predication? In line 291, it was mentioned that the other end-member possesses d18O values ranging from 5 to 15 per mil. I am not sure where the authors obtained these numbers. Can the authors clarify?"

First, end-members were chosen graphically to encompass all our data on Fig. 4 and 5. This is the reason why the CAS/PL end-member (which is inferred here) has a $\Delta^{17}\text{O}$ of 0‰ in agreement with marine sulfates $\Delta^{17}\text{O}$. Then, we looked for sources in the literature that match those end-members. The way we chose our end-members is clarified in the text. Concerning the d18O, the 34S-depleted end-member (anthropogenic sulfur) has a variable 18O from approximately 5 to 15‰ to encompass all our black crusts graphically. We chose to limit this mixing calculation to two end-members (explaining the large d18O range for An end-member) because the variation of oxygen isotopes (d18O and $\Delta^{17}\text{O}$) reflects various oxidation pathways.

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"The definition of anthropogenic emission endmember (d34S = -3 per mil) is also unclear and may be problematic. It is well-known that d34S values of anthropogenic emitted sulfur are highly variable. This fact is also noted by the authors in lines 314-316. Given that the 34S value could be from -30 per mil to 30 per mil as cited by the authors, I am confused why the value of -3 per mil was selected. I checked Montana et al. (2012) cited by the authors but cannot find the value of -3 per mil."

Anthropogenic sulfur, with its wide range of d34S from -30 to 30‰ can match both end-members but the sulfate aerosols in Paris measured by David Au Yang during his PhD show a narrow range between -0.57 and 11.33‰ (L333-334) and the vicinity of the plaster and occurrence of CAS with 34S-enriched sulfates cannot be neglected as potential sources. Therefore, we decided to model a mixing between two different sources, 34S-enriched and depleted. We took an An d34S end-member of -3‰ because it enables to encompass all our data graphically, it is the same as reported by Montana et al. (2008) (and not Montana et al., (2012), sorry for this mistake) and close to the most negative value measured in Paris (d34S = -0.57‰. To highlight the sensitivity of our calculation to the somewhat assumed d34S of -3‰ we also calculated mixing proportions with an An d34S end-member of -10‰ encompassing the black crusts of Antwerp supposed to trap higher amounts of anthropogenic sulfur (Torfs et al., 1997; L350-352).

4) "I would like to point out a possibility that pyrite could be oxidized by H₂O₂ or even O₃. This is shown by a recent talk in the AGU fall meeting this month(<https://agu.confex.com/agu/fm19/meetingapp.cgi/Paper/597703>). I am not saying that such oxidation pathways play a dominant role in the authors' samples, but the authors should carefully consider this possibility. One can also argue that the authors' samples are mixed by three end-members (CAS/PL, anthropogenic sulfur, and oxidized pyrites)."

We added this information in the manuscript L325-330. Pyrite oxidation by O₃ could explain $\Delta^{17}\text{O} > 0\text{‰}$ for the 34S-depleted end-member but we argued that so far the

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fluxes of common atmospheric constituents for pyrite oxidation, i.e. O₂ and H₂O, are still higher than O₃ amounts.

5) "The D17O calculation in line 397 is wrong. The measured D17O value is also controlled by other oxidants such as OH radical and O₂. In the calculation done by the authors, the estimated contribution of S(IV)+O₃ oxidation pathway is just the lower limit as the authors assume the S(IV)+H₂O₂ reaction is the only other oxidation pathway. The authors can also estimate the maximum contribution of S(IV)+O₃ oxidation pathway by assuming no contribution from H₂O₂."

In the new version, we removed this calculation because the main point was only to highlight the presence of atmospheric sulfates in black crusts ($\Delta^{17}\text{O} > 0.65\text{‰}$).

6) "Line 514: This is a misleading statement. It is an "interpretation" instead of "observation". Non-zero D33S value is still a prediction and has not been confirmed by any measurement yet. It is important to do such measurements in the future to test the authors' prediction though."

This misleading is corrected in the new version L463-466: "SO₂ in the Paris basin still has to be measured to confirm this assumption but so far, this could be consistent with the interpretation that non-zero $\Delta^{33}\text{S}$ -values of residual/background atmospheric SO₂ are erased by anthropogenic SO₂ having zero $\Delta^{33}\text{S}$ -values (Au Yang et al., 2019) moving towards the local source(s) of anthropogenic SO₂."

7) "In the discussion of magnetic isotope effects, the authors suggested that they cannot rule out the effect of micro-organisms. If isotopic compositions in black crusts were linked to magnetic isotope effects from microbial activities, how do the authors explain the D17O data?"

We think that oxygen isotope compositions are not affected by MIE because we should otherwise expect at least that the most ³³S-depleted sample corresponds to the most ¹⁷O-depleted-values, which is not the case (added L475-476). Furthermore, sulfates

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from black crusts sampled in Paris have $\Delta^{17}\text{O}$ similar to sulfate aerosols also gathered in Paris by Lee et al., (2002), suggesting that oxygen isotopes record an atmospheric process, not affected by MIE on the surface of building stones.

8) "I suggest putting all legends on all figures. It is difficult to check the caption one by one."

We put all legends on all figures as it was suggested.

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