

***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 first referee were important to improved our manuscript. We almost followed all of them.

1) "Some of the discussion parts are unnecessarily lengthy especially considering the insignificance of the problems in question. The proportion of natural vs. anthropogenic estimates have been done before and usually bear a large uncertainty and is not a

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critical problem. Those lengthy discussions and estimates are diluting the important discoveries in this study. I suggest trying to trim the text down to 50% of the current length. Focus on new things, the  $\Delta^{33}\text{S}$ , and the  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  correlation."

We think that before addressing if  $\Delta^{33}\text{S}$  anomaly lies in a "process" rather than a "source", it is important to check if S and O isotopic compositions are affected by processes (e.g.  $\text{SO}_2$  partial oxidation, gypsum precipitation. . .) even if it only slightly overprint the source signatures. It would otherwise confuse the reader having two sections, one dealing with mixing ( $d^{34}\text{S}-d^{18}\text{O}-\Delta^{17}\text{O}$ ), the other dealing with processes ( $d^{34}\text{S}-\Delta^{33}\text{S}-\Delta^{36}\text{S}$ ). We added our developed reasoning L247-251. Given that  $d^{34}\text{S}-d^{18}\text{O}$  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  $d^{34}\text{S}-d^{18}\text{O}-\Delta^{17}\text{O}$  sections, keeping the discussion about processes even if mixing is the main mechanism and reduced the text by  $\sim 1.5$  pages for this part of the discussion, almost 20% of the 50% asked by the first referee, whereas the second referee leaves us the decision to reduce or not. Furthermore, we added details asked by both referees which does not allow us to reduce the text as much. The discussion is very detailed 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.

2) "I could guess from the text that at least two writers were writing this manuscript. Make sure the English and flow are consistent."

We agree and tried to homogenize the English in the manuscript.

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3) We took into account all the syntactic comments suggested by the referee, not listed here.

4) "Line 26-29: This is inconsistent with the many published negative  $\Delta^{33}\text{S}$  data from Beijing, e.g. Han et al., 2017."

We clarified this aspect, adding L27 that "except for a few samples", sulfate aerosols have mostly positive  $\Delta^{33}\text{S}$ .

5) For the following comments: "Not necessarily going through a  $\text{H}_2\text{SO}_4$  phase" we added "can" L34. "Influent" is replaced by "efficient particles" L39. "Not necessarily distant" we added "a local or more distant source" L46-47. For the oxidants, we used the simplification suggested by the referee that is the three main pathways L47-48.

6) "Line 81: "Intrinsic" is a poor choice here. and Line 225: "extrinsic" and "intrinsic" are not ideal words here."

We agree but we only reported this term because used in the literature by Kramar et al., (2011) and Kloppmann et al., (2011). Because many distinctions exist for sulfate aerosols (primary/secondary; natural/anthropogenic...), we removed the intrinsic/extrinsic distinction in the discussion, only recalling its use in the literature L85.

7) "Line 88-89: Few sulfate samples have been measured for all the 4 sulfur and 3 oxygen isotope compositions together. Thus, this is not a significant thing to say."

We wanted to highlight that this is the first time for black crusts samples. We agree it is not the case for sulfate aerosols and we removed this emphasis L91-95.

8) "Line 105-114: There are numerous conceptual misunderstanding and inaccuracies in these writings. I suggest delete them all. Line 114-115: Some of the deviations maybe still be massdependent under this definition per se. Line 117: I suggest you use 0.5305 for the sake of internal consistency. Note that both 0.515 and 1.889 are the high-temperature limit values for quadruple sulfur isotope system. For triple oxygen isotope system at high-T limit, the exponent value is 0.5305."

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We explained in another way, L110-121, the concept of mass-dependent vs mass-independent fractionation depending on how large is the deviation from the mass-dependent curve, without using the term "anomaly" which was indeed ambiguous. We also applied 0.5305 for 17 (L104, L108 and Eq. 1), specifying that all the used here are the high temperature limit (L108), as suggested by the referee.

9) "Line 158: We had a similar correction factor. This correction will have +/-2‰ error (1 sigma). Sample impurity and therefore  $\text{O}_2$  yield has been the major source of errors. Thus, the actual error for  $\text{d}^{18}\text{O}$  of sulfate could be much larger."

We believe that our correction factor can be applied to all samples without such a significant error because 1) all samples were purified on an ion-exchange resin to get only the sulfates (protocol implemented by Legendre et al., 2017) and 2) the reproducibility between duplicate samples is  $\sim 0.3\%$  lower than the NBS127 reproducibility. If the  $\text{O}_2$  yield was different for one sample, we should notice it with the duplicate uncertainty. We added this explanation L156-159.

10) "Line 228-239: These discussions are not necessary because the Rayleigh process requires sampling from the residues or products of the same reservoir during evolution and the black crust gypsum is not."

Here, we modeled black crusts as the cumulated product, not as instantaneous product. The initial isotopic composition is the same for the whole Parisian basin, and black crusts from different places represent the cumulated products at different residual fraction  $F$ , which is the residual sulfates in water that leached the host-rock. Our gypsum precipitation model is now better specified L254-259.

11) " Line 240-252: I think this is because Harris et al (2012)'s fractionation factors are not for multiple steps with multiple oxygen sources and are only applicable in their particular experimental settings."

We agree that they are applicable in their particular experimental settings but they are

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the only existing parameters so far, we cannot therefore neglect them. We choose to keep our model in the manuscript L260-270.

12) "Line 256, 257, 261 ...: significant digits should reflect experimental error, in the case of  $\delta^{34}\text{S}$ , it should be at most at the second decimal points."

We modified the digits of all  $\delta^{34}\text{S}$  and  $\delta^{33}\text{S}$  (second decimal points).

13) "Line 393-402: This  $\text{O}_3\text{-H}_2\text{O}_2$  proportion exercise is not only too simplified but also invalid because you did not consider the contribution of Fe-Mn catalyzed oxidation by  $\text{O}_2$  in aqueous condition, a pathway that is known to be significant."

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

14) "Line 444-445: The sentence "resulting in negative  $\delta^{33}\text{S}\text{-}\delta^{36}\text{S}$  but not low enough to explain  $\delta^{33}\text{S} < -0.2\%$ " is ambiguous here."

We wrote it in another way L394-397, specifying the model on figure 6 "resulting in slightly negative  $\delta^{33}\text{S}\text{-}\delta^{36}\text{S}$  that could not explain the  $\delta^{33}\text{S}$  as low as  $-0.34\%$  measured in black crusts (yellow frames on Fig. 6)".

15) "Line 521-523: I'd rather see this "microbial ..." sentence deleted entirely."

As we do not know the reaction leading to MIE in black crusts, we think it is important to suggest some possibilities that rely on previous observations. We did not accordingly delete this sentence.

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