

***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.***

**Anonymous Referee #1**

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Black crusts contain sulfate of atmospheric deposition integrated over a period of time. They are an archive of atmospheric sulfate, some of which are secondary atmospheric sulfate derived from the oxidation of  $\text{SO}_2$  (mostly). This study sampled a set of black crusts among Paris metropolis and discovered that many of the sulfate samples bear negative  $\Delta^{33}\text{S}$  values while nearly invariable in the  $\Delta^{36}\text{S}$ . This prompted the authors to conclude that black crusts or associated heterogeneous oxidation of  $\text{SO}_2$  may have been the “missing” pool of the  $\Delta^{33}\text{S}$ -negative sulfur being sought to balance the observed, largely  $\Delta^{33}\text{S}$ -positive atmospheric sulfate aerosols. The authors also specu-

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lated the mechanism to be a magnetic isotope effect associated with heterogeneous radical reactions. This is an interesting discovery that may provide clues to the mysterious  $^{33}\text{S}$  anomalies in modern atmospheric sulfate. However, the current draft could benefit from some major revisions before being accepted for publication. 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 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. 2. I could guess from the text that at least two writers were writing this manuscript. Make sure the English and flow are consistent. 3. Some of the specifics listed below are syntactic and some are conceptual and should be dealt with in diligence. Line 26-29: This is inconsistent with the many published negative  $\Delta^{33}\text{S}$  data from Beijing, e.g. Han et al., 2017. Line 33: Not necessarily going through a  $\text{H}_2\text{SO}_4$  phase; “they” should be “that”. Line 38: “influent” is not a good word here; delete “gases”. Line 46: not necessarily “distant”. Line 51: To many, there are three pathways: gas (homogeneous), aqueous, and heterogeneous (surface). Line 54: characterizing Line 81: “Intrinsic” is a poor choice here. 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. 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 mass-dependent 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. Line 158: We had a similar correction factor. This correction will have  $\pm 2\%$  error (1 sigma). Sample impurity and therefore  $\text{O}_2$  yield has been the major source of errors. Thus, the actual error for  $\delta^{18}\text{O}$  of sulfate could be much larger. Line 160: Change “during” to “for”. Line 162: precipitated as Line

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185: Being consistent with . . . Line 193: delete words after and including “highlight”, partly because “anthropogenic emissions” is poorly defined. Line 197: change “can” to “may”. Line 215: delete “;”. Line 222: etc. Line 225: “extrinsic” and “intrinsic” are not ideal words here. 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. 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. 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. Line 297-298: Check the English Line 322: you meant “between a less variable” instead? Line 334-335: A very confusing sentence. Line 372: Delete “implying a lower  $\text{pCO}_2$  and/or a higher flux of sulfide re-oxidation in sediments”. It’s a distraction. 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. Line 444-445: The sentence “resulting in negative  $\Delta^{33}\text{S}$ - $\Delta^{36}\text{S}$  but not low enough to explain  $\Delta^{33}\text{S} < -0.2\text{‰}$ ” is ambiguous here. Line 483: “than”, not “that”. Line 521-523: I’d rather see this “microbial ...” sentence deleted entirely. Line 564: Change “little” to “poorly”. Line 565: change to “whose”. Line 570: delete “the” before “figure 8”.

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