

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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Small but significant mass-independent fractionation anomalies of quadruple sulfur isotopes (S-MIF) have been widely observed in today's atmospheric sulfate aerosols. Similar isotopic signatures were also observed in ice and lake sediment records. These observations were somehow unexpected in that they are in contrast with the traditional assumption that S-MIF in sulfate aerosols are ONLY produced in the stratosphere by UV-induced photochemical reactions of SO₂. The fundamental processes leading to such “unexpected” S-MIF signature are being highly debated recently and several

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mechanisms have been proposed. More measurements in the modern atmosphere and in geological records containing deposited atmospheric sulfur are important for testing existing predictions and for a more precise understanding of S-MIF chemical physics and atmospheric sulfur cycle.

In this manuscript, the authors present a new set of quadruple sulfur isotope data in gypsum-forming “black crusts”. Measurements of triple oxygen isotopes in these sulfate samples suggested that most sulfates samples are of atmospheric origins. An interesting finding is that most quadruple sulfur isotope data are characterized by negative D₃₃S values (from -0.34 per mil to ~0 per mil), a pattern different from most observation in the past. The variation of D₃₆S values (from -0.7 per mil to -0.2 per mil) is however relatively small compared to previous studies. The authors interpret these observations as a signature of magnetic isotope effects during SO₂ oxidation on carbonate, although the effect was not tested by laboratory experiments and a detailed mechanism was not proposed. They then argue that such reaction will lead to positive D₃₃S values in residual SO₂, which explain the positive D₃₃S values in most atmospheric sulfates. Overall, the isotope data are novel. The interpretation, which is subject to further discussion and validation, is testable. This work is deserved to be published in ACP. I have several suggestions as follows to improve the manuscript before its final publication.

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, 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

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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.

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.

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? 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. I suggest the authors to check previous d34S measurements of SO₂ and sulfate in the same studied region, if there is any, and use those data as end-members. The uncertainties should be also considered and briefly discussed.

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

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(<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).

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.

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.

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?

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

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