Interactive comment on "Sulfur isotope fractionation during heterogeneous oxidation of SO$_2$ on mineral dust" *by* E. Harris et al.

E. Harris et al.

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We thank the three anonymous reviewers for their helpful comments on the paper. We will discuss below the changes that have been made in response to the reviewer's comments. The changes will be presented in the order they appear in the manuscript.

- P2305 L13: 'on to' was changed to 'onto'.

- P2309 L5: The paragraph was given a subheading of '3.1.1 Mineral dust used in experiments' to better reflect what is actually discussed, as requested by Reviewer #1.

- P2311 L17: Reviewer #2 requested more detail on the potential for background

sulfate production in the surface reaction experiments. The lamp emission spectrum is compared to the absorption spectrum in Figure 2 to show that photolysis of SO$_2$ and O$_3$ will be negligible as the absorption cross sections for both species are extremely low; J_{SO_2} cannot be calculated as the actinic flux is unknown. A sentence was added to P2311 L17 to clarify the lack of background oxidation pathways:

"...Analyzer (Model 49C). The rate of gas-phase SO$_2$ oxidation by O$_3$ is negligible (Li et al., 2006), no aqueous phase is present, and photolysis of SO$_2$ and O$_3$ is negligible, thus surface reactions will be solely responsible for sulfate production. Each experiment was done..."

- P2314 L16: A definition of 'untreated' was added at the first usage: "The untreated Sahara dust (ie. the Sahara dust as collected on the Cape Verde Islands and not subject to experimental exposure to SO$_2$) contained..."

- P2319 L11: The abbreviations used in Section 5 are all defined in Table 2; this is now stated in the text of Section 5.1 to avoid confusion. 'and' was also changed to 'at': "Sulfate production on the dust surface at subsaturated humidity was quantified as described in Sect. 3.2, and the results are shown in Fig. 4 (abbreviations are defined in Table 2)."

- P2319 L12: The concentrations are linearly extrapolated to 8 hours. In the text, 'estimated' was changed to 'linearly-extrapolated' to make this more clear: "Experiment lengths ranged from 6.3 to 9.2 h, so the results shown were corrected and represent the linearly-extrapolated concentration after exactly 8 h of experimental time, to factilitate comparison between experiments."

- P2319 L20 - P2320 L2: Reviewer #1 noted that the SEM results in Figure 4 show no significant sulfate production except in the presence of O$_3$, UV light and humidity; the NanoSIMS count rates, which are more sensitive, show significant sulfate production in all experiments. This is now clarified in the text:

"The count rates observed during NanoSIMS analysis show an increase for all treated samples compared to the control, and are also much higher for MDRHO3hv, in agreement with the SEM samples. Thus, sulfate production is significant, fairly slow and similar for all experiments except MDRHO3hv: this combination of conditions saw much more sulfate produced..."

- P2321 L14-19: Reviewer #1 requested that the word 'factor' not be used in Section 5.3, as it is confusing when used in the same paragraph as fractionation factors. To address this, in Section 3.4 'Positive Matrix Factorization', the word 'factor' was put into inverted commas to emphasise that it is specific terminology associated with the PMF model. At the beginning of Section 5.3 (P2321 L14-19) the factors were defined and all subsequent instances of the word 'factor' in reference to PMF changed to 'mineral assemblage':

"Four 'factors' were identified from the PMF analysis. Each 'factor' is not representative of a single mineral, but rather of a group of minerals that, acting together or separately, cause the same isotopic fractionation during sulfate formation; thus the 'factors' will hereafter be referred to as 'mineral assemblages'."

- P2323 L26: The percentage of sulfate production due to Mineral assemblage 1 is now stated in the text of Section 5.3.1: "...the highest reactivity of any mineral assemblage - contributing 85% of sulfate production - which is in agreement with observations...". All the rates and percentage contributions are summarised in Table 4.

- P2325 L3: 'enriched in ^{32}S' has been replaced with 'depleted in ^{34}S'.

- P2325 L3-20: Some inconsistences were corrected in the discussion of Mineral assemblage 2:

L3-5 'The elemental composition suggests the mineral assemblage represents feldspar and a component containing Fe such as mica or hematite, both of which

are known to be a common constituent of Sahara dust...'

and L8-20 'Uptake to this factor is relatively slow, and the isotopic fractionation is opposite in direction the other factors, which have more basic character, thus uptake to Factor 2 appears to be dominated by less basic sites associated with Al. This is consistent with the expected effects of ageing during transport, which will remove alkali components, leaving aluminium oxides exposed. The Fe ions in the minerals associated with feldspar will increase the acidic character. Although Fe^{3+} can catalyse S(IV) oxidation (Herrmann et al., 2000), this reaction pathway will be insignificant without an aqueous phase. The adsorption of SO_2 to Al_2O_3 results in sulfite with significantly different IR absorption bands to, for example, MgO (Goodman et al., 2001), which explains the strongly negative isotope fractionation that is very distinct from the other factors.'

- P2329 L10: 'is' has been removed between 'rate' and 'of'.

- P2331 L9: A reference to a new study by Alexander et al. (2012) has been added to Section 6: Comparison to field studies:

"...until some days after emission (Dentener et al., 1996). A recent study by Alexander et al. (2012) considers the O-isotope composition of sulfate on one marine sample with an air mass of Saharan origin. The results show the importance of the O_3 oxidation pathway, while oxidation on the dust surface and in leachate in the aqueous phase in clouds contribute a small but significant amount of sulfate; the sulfur isotope fractionation factors presented in this study would be an ideal way to complement the $\Delta^{17}O$ analyses presented by Alexander et al. (2012). The fractionation factors presented in this study..."

- P2332 L18: The fractionation factors for oxidation by OH, H_2O_2 and O_3 were added to the conclusion so that a global view of all relevant fractionation factors is given in the paper: "...by OH and oxidation by O_3 and H_2O_2 in the aqueous phase ($\alpha_{OH} = 1.0087 \pm 0.0007$ and $\alpha_{aq} = 1.0167 \pm 0.0019$; Harris et al. (2012))."

- Figure 4 caption: 'y-axis' has been changed to 'x-axis'.

- Reference list: There were some problems generating the reference list in the Discussion Paper. These problems do not appear in our version of the final manuscript. These problems may be caused during compilation of bibtex. We will alert the production office to these problems and will check the galley proof carfully.

- Reviewers #2 and #3 requested more information regarding the leaching protocol. We have added the following details:

  P2309 L18: The pH of the leaching solution was added to the text:

  "...two days in MilliQ water. The solution was not open to the atmosphere during leaching, thus the pH of the leaching solution was 7. The liquid phase..."

  P2309 L20: More details were added regarding the handling and storage of the dust leachate:

  "...when the solid phase is removed (Cohen et al., 1981; Rani et al., 1992). The leachate was then stored in an air-tight jar in the dark at room temperature and used within two weeks."

  P2309 L20: The efficiency and leaching conditions were discussed:

  "The leaching protocol was chosen to mimic ambient leaching, without sonication or heating, and provide a first estimate of sulfur isotope fractionation during aqueous oxidation in mineral dust leachate. No chemicals or buffers were added to the solution, in order to minimise interferences such as unwanted aqueous oxidants, although in the ambient environment it is likely that the cloud water in which leaching occurs will contain a number of other species. The concentrations of Al, Ca..."

- Reviewer #3 commented that traditional isotope analysis techniques may have been an advantage to improve precision in results. Traditional isotope analysis

  would not have been suitable for the surface oxidation experiments as it would have masked the mineral-specific effects and introduced problems with background and extraction. Traditional techniques may have increased precision in the aqueous experiments, however although the amounts of sulfate (<1 μg) were 'large' with regards to a NanoSIMS analysis, they are still at the lower limit of traditional measurement techniques and therefore require sophisticated systems and extraction techniques that are not readily available (eg. Ono et al. 2006). Thus, NanoSIMS was the best-available technique for measuring isotope ratios in these experiments.

- Reviewer #2 requested more information on blanks used in the experiments.

  P2310 L9: The aqueous reaction system was investigated in detail by Harris et al. (2012) and is therefore not discussed in detail in this paper; a reference to the previous study and an explanation was added to the text at P2310 L9 to clarify this point:

  "...prior to sample collection. The experimental system and potential interferences were examined in detail by Harris et al. (2012) and will therefore not be discussed in this paper. Background sulfate sources considered in Harris et al. (2012), such as impurities in the water, have a negligible effect on the results as oxidation in the leachate is very efficient and a large amount of sulfate product is produced."

  P2311 L1: Untreated controls were used to monitor background sulfate in the surface oxidation experiments and the SEM and NanoSIMS results for these samples are already detailed throughout the paper. A sentence was added to the Methods section at P2311 L1 to make this more explicit:

  "...with abbreviations that will be used throughout this paper. Untreated dust was also examined as an experimental control to monitor background sulfate. A high power LED..."

- Reviewer #3 pointed out that the possibility of mass-independent fractionation was not discussed in the paper. δ^{33}S was measured during all analyses and all measurements showed mass dependent fractionation. This was added to the paper:

P2304 L17: '...relative humidity. All the investigated reactions showed mass-dependent fractionation of ^{33}S relative to ^{34}S.'

P2318 L18: '...at 19°C. Fractionation was mass-dependent with regards to ^{33}S. The majority...'

P2321 L22: '...fractionation factor α_{34} of the mineral assemblage. Fractionation was mass-dependent with regards to ^{33}S for all samples, thus fractionation of ^{33}S will not be discussed further.'

References

Alexander, B., Allman, D. J., Amos, H. M., Fairlie, T. D., Dachs, J., Hegg, D. A. and Sletten, R. S.: Isotopic constraints on the formation pathways of sulfate aerosol in the marine boundary layer of the subtropical northeast Atlantic Ocean, J. Geophys. Res., 117, D06304, doi:10.1029/2011JD016773, 2012.

Dentener, F. J., Carmichael, G. R., Zhang, Y., Lelieveld, J. and Crutzen, P. J.: Role of mineral aerosol as a reactive surface in the global troposphere, J. Geophys. Res., 101, 22869-22889, 1996.

Goodman, A. L., Li, P., Usher, C. R. and Grassian, V. H.: Heterogeneous uptake of sulfur dioxide on aluminum and magnesium oxide particles. Journal of Physical Chemistry A, 105, 6109-6120, 2001.

Harris, E., Sinha, B., Hoppe, P., Crowley, J. N., Ono, S., and Foley, S.: Sulfur isotope fractionation during oxidation of sulfur dioxide: Gas-phase oxidation by OH radicals and aqueous oxidation by H2O2, O3 and iron catalysis, Atmos. Chem. Phys., 12, 407–423, doi:10.5194/acp-12-407-2012, 2012.

Herrmann, H., Ervens, B., Jacobi, H. W., Wolke, R., Nowacki, P. and Zellner, R.: CAPRAM2.3: A chemical aqueous phase radical mechanism for tropospheric chemistry, Journal of Atmospheric Chemistry, 36, 231-284, 2000.

Ono, S., Wing, B., Johnston, D., Farquhar, J. and Rumble, D.: Mass-dependent fractionation of quadruple stable sulfur isotope system as a new tracer of sulfur biogeochemical cycles, Geochimica et Cosmochimica Acta, 70, 2238-2252, 2006.