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Interactive comment on “SO_2 photolysis as a source for sulfur mass-independent isotope signatures in stratospheric aerosols” *by* A. R. Whitehill et al.

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This manuscript is a new, important and a convincing piece made by the Ono’s group regarding the source and origin of the S-MIF in modern sulfate aerosols. After working on the topic for years, the authors reached an impressive mastering of the SO2 photolysis experiments and their related MIF effects. The paper is really well written exhaustive covering experimental data, molecular dynamic, kinetic chemistry and atmospheric applications. Thus I highly recommend the publication in ACP. This is probably the most accomplished work on the subject, applicable to the present atmosphere. While not yet in direct link with the Archean atmosphere, it is definitely a significant step toward that direction. The present results will certainly help to constrain the structure and composition of the Archean atmosphere, which is currently our main unknown the completely understand the Archean data. Nevertheless, I still want to emphasis that this study should not be considered as the final answer to the issue and more photolysis experiments will be needed to have a complete picture on the topic. I have only few minor comments and questions before the paper can be published in acp. Note that molecular dynamic is not my field of expertise and thus I did not critically review this part of the paper and thus unable to judge the quality of the work and the limitation of the interpretation of the calculations, even if the models used are pretty standard in the field.

1/ recently Gautier et al. showed at Golsdschmidt2014 a new set of ice core data. Reporting the data in a ∆33S vs ∆36S plot, the slope obtained is more around -1.9 than -4 as claimed by the author. Can the author comment on that? can the slope of -2 been a mixture of photodissociation and photoexcitation or the result of wavelength dependency effect?

2/Is the data obtained from the full spectra of the Xe lamp (positive ∆33S negative ∆36S) consistent with XS and spectral flux of the lamp?

3/ Is there any explanation for the large difference observed between replicated experiments? Large variations are observed for same experimental conditions.

4/ Xe or D2 are significantly different than the solar spectra. How this can impact the obtained results and comparison with ice core data?

5/ Why quenching of O1D is assumed to be instantaneous? Quenching is known for O2 and N2 and should have been easy to implement in the model or to check the validity of the assumption

6/ is it possible than the high barrier encountered for the TS4 on the singlet PES be lowered by heterogeneous chemistry? can this be explored by the molecular dynamic calculation?

7/ Why the authors have not used the TUV model for the calculation of photolysis rates in the atmosphere (http://cprm.acd.ucar.edu/Models/TUV/)? This model has became a standard tool in atmospheric photochemistry

8/ Wording about the SO2 self-limiting effect is ambiguous as it is always the case for any absorbing molecules which by essence limit the radiation for further absorption by the same molecule. I guess they want to say here that taking into account the high concentration of SO2, self-shielding can dominate over shielding by other molecules (eg O3)

9/ I'm not convinced that self-shieling will decrease the significance of R6 with respect to OH oxidation pathway as OH will also be impacted by the shielding effect but most importantly by the buffering effect (i.e. titration of OH by SO2)

10/The author should add a table displaying the instantaneous fractionation factors. This fundamental for future atmospheric modeling and easy to extract.

minor remarks

SO2 and even more O or SO are pretty aggressive compounds. Was there thermocouples protected from oxidation? Can they have reacted with the sulfur compounds?

Why the setup for photodissociation and phototexcitation are different, in particular the SO2 partial pressure (0.1 kPa vs 1 kPa) or quartz window vs a water IR filter, making the comparison between experiments more difficult.

Can the spectra of the D2 be given? Can the shorter wavelengths open another exit channel?

Do the author have any idea of the humidity present in the cell/flowing gases and thus have an idea of the lifetime of SO3 to check if their assumption of collecting 100% of SO3 makes sense?

Can the authors give the lamp and filters used in caption tables?

Many times eq(5) cited in the text actually corresponds to eq(4).

Table 4: column 4 yield/umol S, technically this is not a yield but an amount

Why in figure 3, the LP experiments show a small MIF when table 3 displays a large effect for the photoexcitation?

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 23499, 2014.