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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Multiple-sulfur isotope effects during photolysis of carbonyl sulfide" *by* Y. Lin et al.

Y. Lin et al.

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Response to Dr. Savarino:

>This is an interesting paper that deserves to be published after minor corrections and clarifications The manuscript tries to answer three different questions, namely the isotopic fraction factor of OCS photodissociation, the source of the sulfate aerosols in the stratosphere, and add another piece of the puzzle in the long run to isolate the causes of the sulfur isotope anomaly found in sedimentary Archean rocks and volcanic stratospheric sulfur compounds. Audience thus surpasses just the regular isotope field. The MS is serious, clear, well organized and presented. I don't see any major flaws, errors, wrong presentation, improper reference/citation or mistakes that could prevent its publication.

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Reply: Thank you for your comments.

> Few general comments: I think the authors are overestimating the accuracy of the "blue" shift or the TS calculation. These are the biggest uncertainties in their manuscript and their interpretations and conclusions should take this into account, especially for the source of SSA. Author should re consider their interpretation/conclusion in the light of this comment and keep these uncertainties in mind when rephrasing.

Reply: ZPE-shift method was simply used to compare our experimental result with this simple model. It was quantitatively agreed that photolysis does not produce very large (>70 per mil) isotope effect, and it predicted relatively larger isotope effect for >285 nm comparing to that for <285 nm. However, the conclusion relied on the experimental results, and not on ZPE model.

>One way to reduce their uncertainties will be to find a way to scavenge S before it can further reacts with OCS. Did they try to use O2? As long as SO2 formed is kept negligible its should be fine, even if it is not the case, as long as no S exchange occurs between OCS and S/SO/SO2, following just OCS should be enough to deduce the fractionation factor.

Reply: Using O2 is an interesting suggestion since O2 + S reaction appears to be fast enough to compete with OCS+S reaction. The product SO2 does have high cross section at around 220 nm so that this is a bit complicated though. Adding ethylene may work better.

>The last general comment concerns the UV range they have tested. Looking at the Farquhar's experiment on SO2, I'm wondering if a huge and large effect will not appear during OCS photolysis but not in the weak absorption band but the strong band that exists deeper in the UV, lower than 180 nm, exactly as SO2 which did not display a strong S-MIF with the Xe lamp but a huge one at shorter UV.

Reply: Agreed. However, photolysis under <180 nm is not very relevant for the Earth's atmosphere due to absorption of this short UV by H2O, CO2, etc.

Minor comments/questions:

>Page 14234 line7: I don't like the term "isotope effect", the usual term is "isotope fractionation constant" which point to a value, effect is more general and process oriented.

Reply: The term should be "isotope enrichment factor ε".

> Page 14234 line18: How the 10 ‰ is calculated? Difference in slope (linear to go faster) is 0.019, to get a difference of 10 ‰ in cap33, you need 500 ‰ fractionation in del34. Seems too much.

Reply: This 10 ‰ was for the isotope effect (for the ratio 34S/32S), and was not the MIF. "for 34S/32S" is added in line 18.

>Page 14235 line 14: change "carbon dioxide" to greenhouse gases.

Reply: "carbon dioxide" is changed to greenhouse gases.

>Page 14235 line 15: change "volcanic SO2" to SO2 (natural and anthropogenic).

Reply: Agreed.

>Page 14235 line 25: missing "and" between del34 and "the UV".

Reply: "δ34S" is changed to "the δ34S fractionation during".

>Page 14237 line 1: Say how this lamp compares to Sun especially in the UV range of interest, and even if the figure 2 displays it.

Reply: This below is added to the caption of Fig. 2: Xe lamp used in this study has higher photon flux compared to solar spectrum by about a factor of 20 for the region between 190 and 270 nm.

>Page 14237 line 3: Say if these flux are measured or given by the manufacturer.

Reply: The fluxes were given by the manufacturer (page 14245 line 4).

>Page 14237 line 11: Is this column suitable for SO2 separation? OCS contains no SO2? This is important for the rest of the MS (see below).

Reply: Yes, it does separate SO2. There was no SO2 detected, however, detection limit may not be high for GC.

>Page 14237 line 15: Do the authors have any idea how S deposition on the window can affect the photolysis rate?

Reply: We observed by our spectrometer that the deposition of S on the window blocks UV and visible light to some degree. The photolysis rate would be affected. This would not have large isotope effect since the deposited S has very broad spectrum signature.

>Page 14237 line 16-18: It is not OCS neither ZnS that precipitated but S

Reply: The sentence is revised as: The OCS (initial or residual) was hydrolyzed in alkaline zinc solution (0.14 mol/l zinc acetate in 2 mol/l NaOH), and sulfur was precipitated as ZnS. The ZnS was converted to Ag2S by 0.1 mol/l AgNO3 after neutralizing with zinc acetate solution.

>Page 14237 line 20: Is this procedure quantitative to recover all S reservoirs? Nowhere data are provided to prove that no fractionations are associated with the extraction procedure.

Reply: Page 14238 line 1 stated, "Six replicated analyses of OCS yield 2σ standard deviations of 0.26, 0.53, and 1.05‰ for δ33S, δ34S, and δ36S, respectively". This demonstrates that the overall procedure is repeatable at 0.5 ‰ for OCS analysis. Reduction of elemental sulfur by chromium chloride followed the method of Canfield (1986) and was quantitative. Table 1 showed that f values (and also ε) calculated from yield and by mass balance match well, which indicated that analytical procedures were quantitative and without fractionations.

Additional comment is added at page 14239 line 4: The consistency between the 34ε (and also f) values calculated from yield and those from mass balance indicates insignificant isotopic fractionation during analytical procedures.

>Page 14238 line 1: Six replicates of OCS. Be more precise. If it is six times the measurement of the same OCS bulb, I wonder if the SD calculated here can be applied to the normal set up.

Reply: The relevant sentence is revised as: Six replicated analyses of OCS, sampled as initial OCS for different experiments, yield 2σ standard deviations of 0.26, 0.53, and 1.05 ‰ for δ33S, δ34S, and δ36S, respectively.

>Page 14238 line 8: remove x 1000 in the expression.

Reply: $\times$1000 is deleted.

>Page 14239 line 9: As it is explained later, what is important is the quenching effect not the addition of N2 in the cell, change "addition of N2 has.."

Reply: "addition of N2" is changed to "the quenching of S(1D) by N2".

>Page 14240 line 8: change "the factor 1/2 " to "the statistical weight" or something equivalent

Reply: "the factor 1/2" is changed to "the statistical weight".

> 14240 line 9: I don't really see why steady state condition for S will not produce an isotopic fractionation during the reaction. What you can assume is that during SSC S is at isotopic equilibrium (i.e. S follows the evolution of the source with a constant fractionation)) but the overall fractionation depends on all possible combinations; OC32S + 34S, OC34S + 32S vs OC32S + 32S, any reaction forming 34S32S contributes to the overall fractionation.

Reply: This is a simple result of intermediate steady state as it is stated in the manuscript. It can be easily shown mathematically.

>Page 14241 line 11: I found 1/4 and not 1/5 (0.75 x 5 10(-11)/15 10(-11))

Reply: This is not correct because 2/3 of S(1D) is quenched by OCS to S(3P) by reaction R3.

> Page 14246 line 23: There is no SO2 in the cell at the beginning or end of experiment that could explain the 0,538 exponent, for instance?

Reply: It is possible but no indication of SO2 to suggest it.

>Page 14247 line 20: Only the first weak UV absorption band is studied here. What if the OCS displays the same behavior as SO2 photolysis? Almost no effect on the weak band and a very strong S-MIF in the strong absorption band at deeper UV? It is too premature to claim that during OSC photolysis and subsequent reactions the process is MD, as explained by authors in the paragraph that follows. So here precise the UV domain concerned by the MDF.

Reply: It is possible but not relevant in Earth atmosphere since these shorter UV will be absorbed by many molecules before hitting OCS.

>Reference page 14251 line 18: Give the DOI of the Lu et al. reference.

Reply: Lu et al. 2006 doi:10.1063/1.2357739 is added.

References:

Canfield, D. E., Raiswell, R., J. Westrich, T., Reaves, C. M., and Berner, R. A.: The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales, Chem. Geol., 54, 149-155, 1986.

Farquhar, J., Savarino, J., Airieau, S., and Thiemens, M. H.: Observation of wavelength-sensitive mass-independent sulfur isotope effects during SO2 photolysis: Applications to the early atmosphere, J. Geophys. Res., 12, 32829-32839, 2001.

Lu, C.-W., Wu, Y.-J., Lee, Y.-P., Zhu, R. S., and Lin, M. C.: Experimental and theoretical investigation of rate coefficients of the reaction S(3P) + OCS in the temperature range of 298-985 K, J. Chem. Phys., 125, 164329, doi:10.1063/1.2357739, 2006.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 14233, 2011.

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