Authors' Response to Comments

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Received and published: 13 October 2014
Review of: SO2 photolysis as a source for sulfur mass-independent isotope signatures in stratospheric aerosols by Whitehill, Jiang, Guo and Ono

This paper describes a series of experiments into the S-MIF pattern produced by SO2 photochemistry, with emphasis on photolysis. It is asserted that SO2 photolysis is responsible for the S-MIF signal observed in some volcanic sulfate in polar ice cores because some of the SO photoproduct combines with O2 in the atmosphere in a three body reaction to form SO3 which reacts with H2O to produce H2SO4. The rate of this reaction is poorly constrained (the only evidence is one determination in the literature of an upper limit) and an effort is made to estimate it's rate. Stationary points on the SO3 potential energy surface are investigated using quantum chemistry, and a chemical box model is used to interpret the experimental results. The paper describes a well-designed set of experiments and painstaking isotopic analysis. There is a lot of interesting material here that makes it a pleasure to read and a valuable addition to the field. I have a few concerns detailed below that should be addressed prior to publication.

Scientific comments
The Introduction is very well written and gives a readable review of current understanding in the field. In 23501, 23 (page, line) it is stated that the experimentally measured 1% KIE for 34SO2 reaction with OH relative to 32SO2 is incompatible with Castleman's measurement of 1974. First, note that this is a single measurement 40 years ago, good work but it includes some uncertainty. More importantly, the experimental measurement was done in the range of -20 to +40 C and does not include the temperature at which the SO2 + OH oxidation took place high in the atmosphere. One must extrapolate the measured KIEs outside the range of the study without a reason to think the temperature dependence of the KIE would be linear. Overall, given these issues, it is speculative to say the experiment and the field measurement do not agree. Suggest more cautious language - perhaps there is an indication, but nothing as clear cut as the text appears to claim.

Changed to more cautious wording.

There must be some water in the photoreactor, in order to convert SO3 into H2SO4. There is always some water on anything that has been open to the atmosphere, including anything that has not been pumped out under high vacuum for many days. How much water? Was OH produced via water photolysis or O(1D) plus H2O?

Added section discussing water and added HO_x chemistry to photochemical model

23500, 27, why 'requires a high SO2 column density'? Not clearly argued in the text. Please discuss how 'requires' is meant - *does this mean a large amount of SO2 between the place where SO2 is photolysed and the sun, in order to ensure self-shielding? Or, simply that there is enough SO2 present in a plume to ensure a signal?*

Changed to be more specific

23500, 27, why 'an SO2 plume reaching an altitude of 25 km or higher'? This limit seems somewhat arbitrary. According to Figure 8, 20 km should be sufficient. Including uncertainties, could it not simply say, 'above the tropopause'?

Changed to "around 20 to 25 km". The exact altitude depends on atmospheric conditions and requires modeling beyond the scope of the present paper.

For example at 23514, 12. Isotope selective intersystem crossing due to an accidental near degeneracy is a plausible theory with some evidence to back it up. It is an advance to the field. However, it will act at the same time as other mechanisms including selfshielding
and the rate of photoabsorption (isotopologue-dependent cross section), not instead of them. The overall effect will be a combination of the basic mechanisms.

Clarified this section to make it clear that optical isotope effects (i.e. cross-section differences and self-shielding) are also present. Optical isotope effects are definitely important in both absorption regions, but (as shown in Whitehill et al. 2013) cannot explain the entirety of the mass-independent isotope effect in the 250 to 350 nm region.

Section 4.2. The 'Ran-Lyon' model uses isotope-dependent vibrational frequencies to derive shifts, and the isotopologue-dependent absorption cross sections are obtained as shifted versions of the 32SO2 absorption cross section. This approach does not take into account changes in the Franck-Condon factors observed by Danielache et al., or changes in the rotational constants/rotational fine structure. This is important when calculating self-shielding. The agreement with experiment is fine, but keep in mind there is more to the story and the model may have gotten the right answer for the wrong reasons.

Reworded this section to make it clear that the "Ran-Lyons" model is not accurate. However, it produces reasonable results comparable with experimental data (under some conditions) and thus provide a useful tool until better cross-sections at appropriate temperatures are available.

The model and the discussion do not consider HOx chemistry, and they do not consider photochemistry of the reduced sulfur compounds. Polysulfur product is extracted and analyzed, and so some additional reactions must take place: S + S2 + M –> S3 + M; oxidation of reduced sulfur, photolysis of polysulfur species, etc. Any of them could

reasonably
give S-MIF in analogy to the oxygen reactions (for example ozone formation,
ozone photolysis, etc.).

Added HOx chemistry and polysulfur chemistry (up through S_2) to the kinetic model.

Although we have no constraints on water within the system, HOx chemistry does not cause a major difference in the results at reasonable estimates of water (< 100 ppm). Addition of more water increases the estimated rate constant, so it is consistent with our attempts to find a lower bound on the rate.

Under the conditions tested here (5% - 20% oxygen in nitrogen), the model predicts that S and S_2 will be insignificant species, with steady state concentrations of ~100 molecules cm^3 (for S) and $\sim 10^{-8}$ molecules cm^3 (for S_2). Therefore, reaction between S and S_2 will not be significant in the presence of oxygen. This is consistent with the lack of elemental sulfur products recovered in all experiments performed in the presence of O_2.

In Figure 6, for the no oxygen case, why don't the sulfate and
the elemental sulfur show mass balance of the isotopes, equal and opposite D33S? If SO2 photolysis is the source of both S_n (polysulfur) and sulfate, why don't they have the same D33S?

The mass-balance is satisfied by the residual SO_2, which probably carries a negative D33S value. In these open system experiments, in the absence of oxygen, both S_n and sulfate carry positive D33S values. This is consistent with previous experiments in the literature (e.g. Ono et al. 2013 shows both sulfate and elemental sulfur with positive D33S values). They do not have the same D33S values because, in the absence of O_2, most of the sulfate comes from SO_2 + O or SO_2 + OH reactions rather than SO_2 photolysis, as discussed in Section 4.3.

Is equation (7) for the spectral irradiance of the lamp independent of the distance from the lamp? What is the uncertainty in this empirical equation?

The distance between the cell and the lamp has a minor effect on the spectral irradiance of the lamp due to the absorption of oxygen (and some ozone). A brief section is added acknowledging this. Previous studies (Whitehill and Ono 2012) using a similar lamp tested the effects and found that they are important below about 195 nm, but relatively insignificant (in terms of total SO_2 photolysis rates) at long wavelengths.

Unfortunately, the empirical expression is fit from the manufacturer's data and the uncertainty in the measurement is not available. We guess that it is sufficient to estimate the SO_2 photolysis rate to within an order of magnitude or better, but it is impossible to know without measuring it. Uncertainty in the lamp is discussed in Section 4.3 (although a quantitative estimate is not given).

23522, 7, Tunneling of oxygen and/or sulfur should not have any effect at all on the *rates of these reactions. Please omit this throw-away explanation.*

We omitted this explanation.

23522, 27, on the fly transition state hopping calculations would ('in theory') be able to derive rate constants without the need for global PESs.

Added a sentence acknowledging the potential of on the fly transition state hopping calculations. Performing such calculations is beyond the scope of this paper.

Section 4.6. First: Three body reactions get faster as temperature decreases. What is the temperature dependence of R6? Second: The discussion in this section ignores the potential role of photoexcitation – the light flux in the photoexcitation range is much larger than in the photodissociation range. Please include and discuss.

The temperature dependence of R6 is beyond the scope of the present work. Added a paragraph in Section 4.7 addressing possible contributions of photoexcitation to the isotope signatures.

23525, 20, Since the Lyons results are do not give accurate high resolution rovibronic structure, how can they give an accurate prediction of self-shielding? The rotational fine structure is very important for self-shielding.

Removed statement that Lyons results predict results accurately.

23526, section 4.7, given the actinic flux spectrum and the SO2 absorption spectrum, it is beyond doubt that photoexcitation will take place. This process very likely has an isotopic signature. What is there to say that photoexcitation and photodissociation do not occur simultaneously?

Section 4.7 attempts to argue that SO_2photoexcitation alone is not responsible for the anomalous isotope effects and that SO_2 photolysis is important as well. Added a paragraph acknowledging the possible contributions from photoexcitation.

In Table 2, why is there such a large difference between the values obtained in the first and second experiment at each temperature? In each case there is a significant drop in d33S, d34S, d36S. Please discuss. Could S chemistry play a role?

We added a section (Section 4.8 in the revised manuscript) that addresses caveats with the experimental studies and discusses possible sources of variability between duplicate experiments.

Table 3, do the organosulfur product enrichments match the predictions of Danielache et al.?

The results from Table 3 (at lower temperature) cannot be directly compared to the room-temperature measurements of Danielache et al. (2012). Room-temperature experiments under similar conditions are compared to room-temperature cross-sections in a previous publication (Whitehill et al. 2013).

Table 4, it is suspicious that there is a negative trend in k(R6) as the oxygen pressure increases. The model includes O2 pressure and Ox chemistry, so in theory, this trend should not be here. Why is the result so dependent on pO2?

k(R6) results in Table 4 come from the rate estimates in Section 4.3, so they do not explicitly include Ox chemistry. They include only total product formation rate and estimated fraction of product formation from R6 (based on D33S values). In our opinion, the values calculated for pO_2 = 5, 10, 15 kPa are all similar (~1e-37), and it is only at 19.8 kPa that a decrease is observed. This behavior could be due to H_2O limitation on sulfate aerosol formation at higher SO_3 formation rates (i.e. higher O_2 pressures), but this is purely speculative.

Table 5, why are the two runs with each filter (200BP, 250LP) so different in terms of delta values? Please explain.

The two 200BP experiments were performed at very different conditions (300 kPa SO_2 versus 50 kPa SO_2) and that likely explains the discrepancy. The two 250 LP experiments are performed under identical conditions, and yet yields are different by an order of magnitude and isotopic composition is different by a factor of 2. The photoexcitation experiments are challenging and have a very low sulfate formation rate. Additional experiments should be performed to clarify the results from photoexcitation experiments, but is beyond the scope of the present paper.

Table 6. The quantum chemistry results are used to make qualitative arguments and the level of calculations does seem adequate to this task. However, as seen here and in tables 7 and 8, the energies obtained using the different methods are very different. How should we know which one to believe, and is there any way to know that the ultimate method used in this paper is adequate to the task? What are the error bars on the resulting values?

It is true that the energies obtained using different methods are different, implying the difficulties dealing with this challenging system by ab-initio calculations. Among those ab-initio methods used in this work, UCCSD(T) energies should be the most trustworthy based on comparison with asymptotic values and thermodynamic data in Section 3.3.Given the multi-reference feature and non-adiabatic coupling involved in multiple electronic states of SO_3, however, an ultimately definitive evaluation of the reaction profile would need further higher level treatment which is beyond the scope of this paper.

Table 9, I do not see sulfate formation. How much water is there? What are the concentrations of the HOx radicals?

The model was modified to include HOx chemistry. We found that inclusion of

H_2SO_4aerosol formation significantly underestimated total product formation for reasonable values of H_2O, thus suggesting that condensation of SO_3 on the walls of the cell or other aerosol particles might be an important process. Modelling this is beyond the scope of the present paper. Therefore, we focused on the rate of SO_3 formation from different pathways.

Figure 1. Very nice straight line. Does this need to be included, and as Figure 1?

Inclusion of temperature calibration is important for demonstrating that our experiments are robust and that we are testing what we claim to be testing.

Perhaps it could be put in a supplementary infromation file, or better yet, left out. The equation and a short description are all that is needed.
Figure 3, very nice result.
Figure 7, left. The model always predicts increased f_R6 as O2 is increased, yet this is not observed in the experiments. Do you have an explanation? Why should we have believe the model and the resulting rate? The rate is not determined directly, but indirectly, via the model. This introduces many uncertainties (J value, completeness of model), and this difference is yet another indication that the model is not right. (The first, as noted above, was that the value of k varies with the oxygen content).

Our revised model also predicts increased f_R6 values as O_2 is increased, but the effect is smaller than in the original model due to the inclusion of additional chemical reactions. The behavior is quantitatively consistent with our results except for the highest $\%O_2$ value (19.5%). As discussed above, it is unclear why the discrepancy for this value.

Technical comments 23500, 9, add colon: 'the two absorption band systems of SO2: photolysis..andphotoexcitation..'

Changed

23504, 11, better to write 'transmittance at wavelengths longer than 190 nm'. It is not clear if 'above' refers to energy, wavelength, wavenumber, frequency, etc.

Changed

23505, 24, I don't see the need for introducing the nonstandard abbreviation 'DCM' for dichloromethane (by the way, the abbreviation is defined twice in the text). It is used so few times, only on pages 4 and 5, so that if you really must shorten it, why not write CH2Cl2?

Changed to dichloromethane

23509, 19, it is too strict to write '=0'.
There is a range of values that would be considered mass-dependent. Suggest either

’approximately equal’ or to give the range.

Changed to “approximately equal”. Exact values are subject to controversy.

23512, 22, this sentence does not use a
parallel construction as the first have is an expectation and the second half a seeming statement of face. Should the second part rather be, ’but are not expected to reproduce’?

Sentence was removed.

23514, 20, there’s not a clear dividing line between chemistry and physics, so
it’s not clear what is meant here in making a distinction between photochemistry and photophysics. Please rewrite using different terminology.

Changed

23514, 25, it is not clear what
is meant by ’overprinting’. See comment above under scientific comments,

Changed to clarify what is meant

23514, 12.
23529, 5, the rate given here does not agree with the range of values given in the abstract, please be consistent.

Changed from rate to order of magnitude estimate and changed manuscript so that it is consistent throughout.

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Received and published: 17 October 2014

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.

We agree that this study is not the final answer. We hope that this study motivates additional research into this issue.

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?

Added a paragraph to Section 4.7 addressing the possible causes of the discrepancy in D36S/D33S and discussing the possibility that photoexcitation might contribute to the isotope signature.

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?

Comparisons of full spectral Xe photolysis data with cross-sections has been performed previously (Whitehill and Ono 2012, Ono et al. 2013). We added a discussion of the cross sections in Section 4.8 of the revised manuscript.

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

Added a section (Section 4.8) which discusses caveats with the experimental studies. We do not have a satisfactory explanation for the observed differences between replicated experiments except for experimental uncertainties. We hypothesize that it could be due to differences in the trace amounts of water vapor within the system affecting the chemistry in the cell.

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

Added a section (Section 4.8 in revisedmanuscript)where we discuss differences between Xe and D_2 spectra and the solar spectrum.

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

The model is modified to explicitly model include $O(^1D)$ chemistry, as well as additional reactions.

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?

Heterogeneous chemistry could be important but is beyond the scope of the present paper.

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

Calculations were performed in a very simplified manner using a simple radiative transfer model. The purpose of the model is a first-order estimate of the importance of the proposed reaction. It is our hope that future modeling studies can

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)

It is correct that a self-limiting effect due to shielding is important for all molecules. However, the isotope effect also depends strongly on shielding by SO_2 (and possibly other molecules), as demonstrated by Ono et al. (2013). More modeling is necessary to determine the effect of shielding by ozone and O_2 on the SO_2 absorption in this region.

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)

SO2 oxidation by OH is catalytic, i.e. it does not consume HOx. Models vary as to the significance of SO2 loading on HOx and OH chemistry. It will also depend upon a number of other factors, such as the vertical profile of SO2 and HOx species. Such modeling is beyond the scope of the present paper.

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

Exact fractionation factors will vary with temperature and SO_2 column density, as well as other atmospheric conditions (i.e. ozone concentrations, altitude, etc.). For this reason, exact fractionation factors are not given and should be derived from more advanced modeling studies. Attempts to provide instantaneous fractionation factors without knowing the exact position in the atmosphere and atmospheric conditions would be misleading.

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?

Thermocouples were only used to calibrate the cell with pure N_2. We assumed the calibration with pure N_2 is similar to the calibration with a small amount of added SO_2. This is discussed in Section 2.1.

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

The setup for different experiments are different to maximize product formation and minimize the effect of the light source on the internal temperature of the cell. The D_2 lamp has a higher flux in the 190 – 220 nm region (where SO_2 photolysis occurs) and not much infrared radiation. For SO_2photoexcitation, a Xe lamp is used due to the higher flux at longer wavelengths. Because the Xe lamp has a high infrared radiation flux, a water filter was used to absorb the infrared radiation and prevent it from heating the cell. The water filter was not used for photolysis experiments because the windows of the cell absorb significantly below 220 nm. Different SO_2 partial pressures are used due to the different cross-section amplitudes of the two absorption bands. SO_2photoexcitation is an order of magnitude stronger (i.e. higher absorption cross-section) than SO_2photoexcitation.

Can the spectra of the D2 be given?

The spectral structure of the D_2 lamp is estimated in Whitehill and Ono (2012). The D2 lamp used here should have a similar spectral structure but a stronger irradiance (due to it being 200 W versus 30 W).

Can the shorter wavelengths open another exit channel?

The glass used for the cell windows (Corning 7980) absorbs significantly below around 180 nm to 200 nm, preventing chemistry from the higher energy dissociation band (< 165 nm) of SO_2 from occurring under our experimental conditions. In addition, in experiments performed in room air (versus a nitrogen atmosphere), air absorbs almost all the radiation below around 195 nm. This is discussed in Whitehill and Ono (2012).

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?

We do not have constraints on the amount of water within the cell. However, the kinetic model of the cell chemistry is modified to include HOx chemistry and an estimate of the amount of water in the cell is made. Attempts to constrain the amount of SO_3 formation based purely on the $SO_3 + 2H_2O$ reaction produce unreasonably small product formation rates, suggesting additional processes (i.e. heterogeneous processes or wall absorption processes) must be trapping SO_3 in the system.

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

Table 1 summarizes the lamps and filters used in the various experiments for the rest of the tables.

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

This was an error in the conversion from Word to Latex. This will be corrected in the final version.

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

(Absolute) yield is the amount of product obtained in a chemical reaction (in grams or moles), which is what is reported. Therefore, we believe that yield has been used correctly in this case.

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

In the experiments reported in Table 3, 100% of the product comes from $^3SO_2$, so the isotope signature is not diluted. In the results displayed in Figure 3, most of the SO_3

likely comes from the $^3SO_2+SO_2 \rightarrow SO_3+SO$ reaction, which produces mass-dependent SO_3 (see Whitehill and Ono 2012). A small amount of the SO_3 comes from a mass-dependent channel, such as $^3SO_2 + O_2 \rightarrow SO_3 + O$ (Hattori et al. 2013) or $SO + O_2 + M \rightarrow SO_3 + M$ (with SO from $^3SO_2 + SO_2$ reaction). Therefore, the product sulfate from the photoexcitation experiments in Figure 3 are diluted by a significant amount of mass-dependent sulfate.