

Interactive comment on “Large volume sample system for measuring sulfur isotopic compositions of carbonyl sulfide” by Kazuki Kamezaki et al.

Anonymous Referee #2

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This manuscript attempts to address a current technical challenge within the atmospheric S and to some extent C cycle research community. It is clear that quantifying the movement of sulphur between the ocean, atmosphere and biosphere and detailing potential interactions and transformations is highly desirable but unfortunately it is still an extremely difficult task to conduct. Carbonyl sulphide is the most abundant sulphur containing gas in the atmosphere and currently there is much debate about its current sources and sinks. Within this framework the use of COS isotopic tracers might provide insights on this problem and help close the COS mass budget. As pointed out in the manuscript this not only holds interest for the communities working on the S cycle and its interactions with climate through chemical reactions in the troposphere and strato-

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sphere but also those working on the carbon cycle, as COS is a close analog of CO₂ and as such moves between the atmosphere and the biosphere alongside CO₂ during various steps of the photosynthetic pathway.

Consequently the motivation to study COS isotopes is growing and there is a need to overcome a number of technical challenges that limit the application of these tracers to help address the scientific questions introduced above. The first problem is that COS is a trace gas (atmospheric concentration around 500 parts per trillion) with an extremely low abundance of the rare isotope species thus large sample volumes are required for Isotope Ratio Mass Spectrometry (around 500 L providing ~10 nmol of COS, in the case of the present study). Secondly, COS is an extremely reactive gas that can be hydrolysed and/or produced rapidly from many surfaces and materials commonly used in gas exchange techniques.

The current study presents a large volume sampling system adapted from a previous system designed for the measurement of volatile halocarbons and hydrocarbons by one of the co-authors of the present study (Bahlmann et al., 2011). This trapping system seems to be capable of tackling the first problem described above by trapping high volumes of air over a relatively short period of time (~100 minutes) and concentrating the air sample in a cryoshipper volume cooled previously with liquid N₂. Details regarding the temperature of the cryoshipper volume are a little vague stated as less than -110 °C. This could be a bit more specific as pointed out by one of the reviewers as other gases may condense at lower temperatures.

The second problem of sample contamination during sampling and sample storage seems to still be an issue that would prevent the routine use of this sampling approach. For instance the authors purge the sampling tubes with high-purity Helium for 12 h before sampling and require high temperatures starting at 160 °C and reaching 330 °C to condition the material. Can this be done in the lab beforehand on a batch of sampling tubes and does the surface remain inert thereafter, if so for how long? Is this step necessary when switching to Sulfinert valves and tubing? I am also curious to know

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how long roughly it takes to process one sample from the pre-conditioning stage to the final analysis of the purified sample on the IRMS?

It was useful to see the change in COS concentration during the preservation period. However, if I understand correctly this is not the experimental set-up for the rest of the data presented in the paper. Can you also plot the preservation data timeline for the non sulfinert experimental set-up please?

Reviewing this as a method paper I feel there were a number of details missing or communicated a bit ambiguously. I am not sure it would be so easy to reproduce this methodology as a result. In particular section 2.1 was rather vague in several places, especially when it came to details of the calibration cylinders being used. Nowhere is the material of any of the calibration cylinders stated. This is not trivial as it is well known that COS is highly reactive and the use of stainless steel or aluminium cylinders for storage of COS standards will cause a drift in the COS concentrations over time and I would assume the isotopic composition too. For example, you state that the calibration cylinders F and G are much lower than that of atmosphere (e.g. G = 160 pmol mol⁻¹), despite being sampled from the atmosphere that should be in the range of 350-500 pmol mol⁻¹. I can only assume that contamination has occurred in the bottles during storage or a scrubber has been used whilst filling the tanks. If I understand these cylinders were filled in 2012 and assumed to represent the global background atmospheric composition. I am keen to know when the calibration curve described in 2.4.1 was actually completed a few days, months or years (2012) before the use of the calibration gases to validate the field measurements for COS concentration and $\delta^{34}\text{S}$? Overall calibration cylinders should be monitored closely over time when filled to see if the cylinder has issues and thereafter regularly checked for drift. It is also recommended to use Sulfinert cylinders or ACULIFE cylinders for COS. Can you confirm whether your calibration cylinders have special wall treatments to minimize contamination of your atmospheric COS gas?

I also think it would be worth discussing a little the caveats surrounding the fragmenta-

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tion IRMS approach for example the potential for O₂ contamination and consequences for the $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ analysis/interpretation.

Finally I think section 3.5 breaks the flow of the paper at the end and think it should rather become section 3.3. This would allow the paper to move out of the technical discussion into the scientific discussion and conclude more naturally. I also feel that the first paragraph of the conclusion is repetition of the results and should be removed. I also agree with the other reviewer that the last paragraph introducing the carbon and oxygen isotopes should not suddenly appear here a bit out of the blue, their measurement is not trivial.

Other details

The application of parentheses throughout this paper needs correcting, just because you quote a number does not mean it should be wrapped in brackets especially if it is integral to the sentence structure e.g. Page 1 line 26 and 27 highlights the type of problem that pops up throughout the manuscript. Please double check all parentheses are appropriate.

Page 1 line 26-27 How can you prove which value is correct? They both seem to be within the range of values for S sources. I would also try to clarify this argument/sentence a bit better. Page 2 Line 8 remove "net ecosystem exchange into" from this sentence. Page 3 Line 11 state the purity of the Helium in % Page 3 Line 12 can you provide more details of the exact S compounds used Page 3 Line 16 what type of commercial cylinders provide details and how often they were measured. Can you also provide details of the compressor used to fill the bottles and any filters that were used on the compressor? Was the air dried before filling the cylinders? Page 3 Line 20 this is a super vague statement can you provide details of how you checked for stability. Page 4 Line 3-4 can you explain how the heating was made and where was this step made in the lab or outside? Page 4 Line 15 removed using what? Page 4 Line 27-28 is the tubing flexible i.e. in a coil or rigid? Page 4 line 29 how is the heating

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achieved? Page 4 line 30 why use steel and not glass. I guess this was later switched to a sulfinert tube? Page 5 line 8 this should be -72oC Page 5 Line 11 where did this injected gas come from? Page 5 lines 22-25 not written very clearly please improve Page 5 line 25 how many replicates were analysed to obtain the precision? Page 6 line 11 size of capillary tube? Page 6 line 9 spec of the diaphragm pump type, flow, pressure? Page 6 line 16 tank ID please Page 7 line 18-20 this sentence does not make sense to me Page 7 line 21-22 ambiguous sentence Page 7 line 26 how? And what does slowly mean? Page 8 line 15 could you explain these OCS blanks please Page 9 line 11 check the units here please and correct Page 9 line 14 hydrolysis requires water were your tanks dry? Page 9 line 28-30 this sentence needs rewritten as it does not make sense to me Page 10 generally there is little statistical testing reported in this paper in general Page 10 this section would really benefit from more results using the sulfinert equipment.

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