

Reply to RC3 from Referee #1

Blue: Referee comment

Black: Our comment

Red: The sentences in our manuscript

To avoid unnecessary duplication, I will restrict my comments to aspects not mentioned by referees #2 and #3 yet.

Reply: Thank you for reviewing our work. We have revised the manuscript according to your comments.

1. The "large volume" aspect needs to be specified – clearly it refers to large volumes of air. Given that only the $^{34}\text{S}/^{32}\text{S}$ ratio could be analysed successfully, the title of the paper should be changed to "Large volume sampling system for measuring the $^{34}\text{S}/^{32}\text{S}$ isotope ratio of atmospheric carbonyl sulfide", or something along these lines.

Reply: Thank you for comment. We changed "large volume" to "large volume air" throughout the revised manuscript; the title was changed to "Large volume of air sampling system for measuring the $^{34}\text{S}/^{32}\text{S}$ isotope ratio of atmospheric carbonyl sulfide" accordingly.

2. Section 2.4.1 should be renumbered 2.4 and renamed "Determination of the OCS concentration".

Reply: This has been corrected accordingly.

3. Section 2.4.2 should be renumbered 2.5 and renamed "Determination of the sulfur isotopic composition of OCS".

Reply: We have corrected this accordingly.

4. Table 2: You should include the results for the sulfur isotope deltas of samples A, F, G and H in the left hand column of this table, for ease of reference. Possibly, you could also present them in a separate table, given that sample G was analysed by Hattori et al. (2015) already, but gave a different result.

Reply: To add $\delta^{34}\text{S}(\text{OCS})$ values for each sample in these tables, we modified Table 1 and Table 2. We added the $\delta^{34}\text{S}(\text{OCS})$ values of samples A–E in Table 1. The $\delta^{34}\text{S}(\text{OCS})$ values of compressed air samples F, G, I, J, and K are presented in Table 2.

5. Table 2: Given that samples B, C and D all seem to have drifted with respect to the reference sample A, how did you ensure that the composition of sample A itself has not changed compared to the previous 2015 paper?

Reply: We corrected $\delta^{34}\text{S}(\text{OCS})$ values of the sample A to VCDT notion again to perform this study. Therefore, after regarding the comments, we compared the $\delta^{34}\text{S}(\text{OCS})$ values between this study and that conducted by Hattori et al. (2015) for samples A and B. We added descriptions of how to correct the $\delta^{34}\text{S}(\text{OCS})$ values to the VCDT notion.

First, we determined the $\delta^{34}\text{S}$ value of sample A by converting OCS to SF_6 ; the SF_6 was measured for $\delta^{34}\text{S}$ relative to the VCDT scale by calibrating against SF_6 similarly converted from IAEA-S-1 (Ag_2S : $\delta^{34}\text{S} = -0.30$ ‰; Robinson, 1993) to SF_6 , as described in Hattori et al. (2015). The $\delta^{34}\text{S}$ value of sample A was 12.6 ‰, which was 1.6 ‰ lower than the data presented in Hattori et al. (2015) with 14.2 ‰. The $\delta^{34}\text{S}$ value of sample B, that was used as a working standard for $\delta^{34}\text{S}$ measurements, was determined by comparison with the $\delta^{34}\text{S}$ value (in VCDT scale) of sample A. The $\delta^{34}\text{S}(\text{OCS})$ value of sample B was (14.1 ± 0.2) ‰ in this study, showing no significant difference with the $\delta^{34}\text{S}(\text{OCS})$ value of sample B (14.3 ± 0.2) ‰ reported by Hattori et al. (2015). Additionally, the OCS concentration in sample B remained unchanged. Therefore, sample B was used as a daily working standard to determine the $\delta^{34}\text{S}(\text{OCS})$ values for all other samples (see Table 1 in the revised manuscript). For samples C and E, in-house OCS by reacting S powder with CO, were different from samples C and E presented by Hattori et al. (2015). However, it is noteworthy that samples C–E examined in this study were different batches of the experiment with Hattori et al. (2015) and not comparable. We regret the confusion this has caused.

We agree on the need to clarify how we determined $\delta^{34}\text{S}$ relative to VCDT for samples. According to the discussion raised above, we added related explanations to section 2.5 in the revised manuscript.

Reference

Robinson, B. W., Sulfur isotope standards, Reference and inter comparison materials for stable isotopes of light elements, in Proceedings of a consultants Meeting Held in Vienna, 1–3 December, 39–46, 1993.

6. 5/31: One could hypothesize that samples F, G and H all started out at the same initial OCS mole fraction and isotope ratio. Adopting this hypothesis, could you please include a plot of their isotope deltas vs. the natural logarithm of the "residual" OCS fraction (i.e. a Rayleigh fractionation plot) to check whether the apparent OCS loss in the cylinders follows a common fractionation constant ϵ ?

Reply: We tried your suggested calculations. However, we did not measure the OCS concentration in samples H, I, J, and K using glass bottles directly. We measured OCS concentration after sampling. Although the OCS concentration measured after sampling might not be robust, we measured the OCS concentration roughly. When we assumed the original OCS concentrations for samples F, G, and K to be the same as sample J, which had the highest OCS concentration, the relation is not on the Rayleigh plot, indicating the samples do not follow a common fractionation constant and/or the origin of OCS concentration and $\delta^{34}\text{S}(\text{OCS})$ values are not the same.

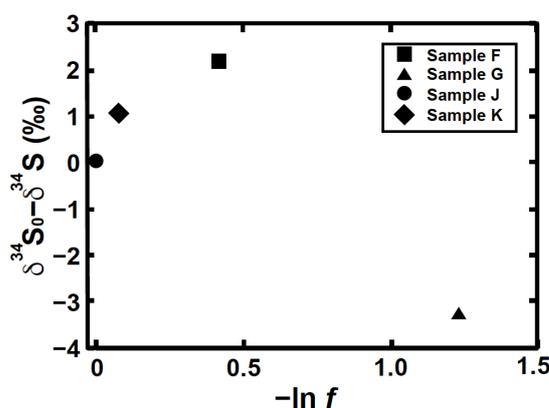


Figure R1: Relative $\delta^{34}\text{S}(\text{OCS})$ value relative to the natural logarithm of the residual OCS fraction. We assumed sample J have original OCS concentration and $\delta^{34}\text{S}(\text{OCS})$ value.

7. 7/26: Please describe in detail how you introduced these aliquots of sample B?

Reply: Sample B was injected manually from the syringe injection port, which is tee with septum equipped before the condenser, over 30 min.

Action: We modified Figure 1 and described in detail in 1st paragraph of section 3.2 as the following: We introduced aliquots of 3 nmol, 6 nmol, 10 nmol, and 15 nmol of sample B over 30 min with a gastight syringe via a syringe port made from a tee union with a septum. The syringe port was placed between the inlet filter and the condenser and the sampling inlet was connected to of high-purity N_2 (> 99.99995 vol. %; Nissan Tanaka Corp., Saitama, Japan) (Figure 1).

8. 8/27: The m/z 33 interference could also be due to NF^+ (e.g. from NF_3).

Reply: Thank you for this comment. We agree that NF_3 is also a possible candidate, as you have suggested.

Action: We added NF_3 to this sentence of the revised manuscript.

9. 11/25: Please state the precision achieved for OCS analysis in this earlier paper.

Reply: We added a new section (section 3.6) to explain a comparison between our methods using GC/IRMS and GC/MC-ICP-MS. We added the comparison of precisions in that paragraph.

10. 22/9: The precision achieved for sample B is not meaningful for these air samples. Please replace the error bars with a more suitable estimate of the precision for an actual air sample.

Reply: Thank you for your critical comment. We estimated the blank effect when the 5 % of contaminated OCS ranging $\delta^{34}\text{S}(\text{OCS})$ value from 3 to 18 ‰ as follows. 5 % of OCS contamination change the accuracy of $\delta^{34}\text{S}(\text{OCS})$ value with -0.3 to $+0.3$ ‰. The precision of our repeated measurement is ± 0.2 ‰. The overall precision of measurement is ± 0.4 ‰. Additionally, the standard deviation of four atmospheric samples we observed was ± 0.2 ‰. Therefore, the $\delta^{34}\text{S}(\text{OCS})$ value for

atmospheric OCS at Suzukakedai campus is $(10.5 \pm 0.4) \%$. We modified the precision and Figure 6 in our revised manuscript.

11. Referee #2 commented on the use of parentheses in your manuscript. The notation " $(x \pm s_x) \%$ " (and similar) follows in fact international guidelines on the SI such as NIST Special Publication 811 2008 Edition "Guide for the Use of the International System of Units (SI)" and the IUPAC Green Book, 3rd edition, p. 151 (section 8.1, example 2; http://www.iupac.org/fileadmin/user_upload/publications/e-resources/ONLINE-IUPAC-GB3-2ndPrinting-Online-Sep2012.pdf). As the journal advocates the use of the SI, no change is necessary.

Reply: Thank you for supporting our presentation of our work. Yes, for this point, we made revisions during the process of revision for AMTD.

Technical corrections

- 2/4: Brühl et al.
Reply: Corrected.
- 2/11: S equivalents
Reply: Corrected.
- 2/17: O(³P) – spin states are not written in italics
Reply: Corrected.
- 3/24: compartments
Reply: We changed “comportments” into “compartments”.
- 3/25 & various occurrences elsewhere: Sulfinert
Reply: We changed all cases of “Sulfinert®” or “sulfinert” into “Sulfinert” throughout the manuscript.
- 5/30: Samples F, G and H
Reply: Corrected.
- 7/23: Add full-stop after system and start new sentence "We sequentially..."
Reply: As commented also by other reviewers, the sentence was not clear.
Action: We rewrote this sentence as 1st paragraph of section 3.2 in the manuscript as follows: **In the developed system, the possibility exists that OCS is lost by passing OCS through GC1. Also, because the flow rate of approx. 50 mL / min was lower than the flow rate of approx. 200 mL / min reported by Hattori et al. (2015), the possibility exists that OCS was lost by Trap 1. Therefore, to assess these possibilities, the following test was conducted. Firstly, 5 nmol of OCS was injected to a system consisting of Trap 2, GC2, and Trap 4 and measured as true value. Then, the same amount of OCS was introduced into the developed purification system and the amount of OCS obtained was compared to true value.**
- 7/25: dependence
Reply: We changed “dependency” to “dependence”.
- 7/31 & 32: Replace full stop after σ with "uncertainty: "
Reply: This point was corrected accordingly.
- 8/26 to 8/28: Remove colon (:) after m/z (e.g. m/z 32)
Reply: Removed all colons (:) with m/z .
- 9/5: USA
Reply: Corrected accordingly.
- 11/5: proofed -> showed
Reply: Corrected accordingly.

Thank you for reviewing our manuscript.

Shohei Hattori on behalf of co-authors.