

Author responses

Reply to RC1 from referee #3

5 **Blue: Referee comments**

Black: Our comments

Red: The sentences in our manuscript

10 The reviewed manuscript presents a method for collection and concentrating OCS (the most abundant atmospheric sulfur species) from air. The concentrated OCS sulfur isotopes are then measured by IRMS. Having such measurement method is an important contribution. The results seems robust, and the manuscript is usually well written.

Reply: Thank you very much for your comments. |

15 The main problem I see regarding the suitability of this method for atmospheric sampling is related to samples preservation. So far, it is shown only for 7 days, which is not always enough to get a sample (i.e. from ship cruise or remote location) back to the lab and to analyze it. Also, no tests were done for preservation effect on isotopes. The authors themselves recognized this point as missing and wrote that “Further investigation of preservation of OCS concentrations and isotopic integrity during the storage of the adsorption tubes with respect to storage temperature and materials of the adsorption tube are currently underway. I recommend that the results from these investigations will be included as part of this paper.

20 **Reply:** We agree that the preservation period of OCS in adsorption tubes is important. During the process of the review, we investigated preservation of OCS in adsorption tubes at 25 °C, 4 °C, –20 °C, and –80 °C. At –80 °C, we found that the $\delta^{34}\text{S}(\text{OCS})$ value is not changed at least up to 14 days. The OCS concentrations are preserved up to 90 days. Therefore, we added data reflecting these experimental results to our manuscript.

25 **Detailed comments:**

Page 1 (abstract), Line 17 – “7 inch tubes (1 cm³)” – better to give both dimensions in cm.

Reply: We apologize for inappropriate expressions because it is difficult to identify what 7 inches was referring to. We replaced “inch” units with “cm”.

30 **Action:** We described the sentence in page 1 line 18 as follows: **adsorption tubes (1/4 inch (0.64 cm) outer diameter, 17.5 cm length, approx. 1.4 cm³ volume).**

Page 1 (abstract), Line 17 “preserving samples” – need to add “up to 7 days”, or to whatever the new investigations show.

35 **Reply:** As we replied above, we have confirmed the preservation of OCS amount and its $\delta^{34}\text{S}(\text{OCS})$ values in Sulfinert-treated adsorption tubes at –80 °C up to 90 days and 14 days, respectively.

Action: We added “**the OCS amount and $\delta^{34}\text{S}(\text{OCS})$ values at –80 °C, respectively, for up to 90 days and 14 days,**” here.

Page 1 (abstract), line 20 – should be “lack of diurnal variations”.

40 **Reply:** We replaced “No significant diurnal variation” with “**lack of diurnal variation**” here.

Page 1 (abstract) line 20 and Page 11 line 6 – It appears here as this method enables measurements also of ³³S in air samples. In fact, this has worked out only for standards, and an interference prevented measuring this in air. Please correct.

45 **Reply:** As you have pointed out, the ³³S for atmospheric OCS was not measured. Therefore, we deleted the precision of $\delta^{33}\text{S}$ and $\Delta^{33}\text{S}$ values for atmospheric OCS in the *Abstract* and *Conclusion* (summary).

Page 1 (abstract) – Portability is reported here based on the sample tubes. But the size and weight of the sampling system is also a main issue. Please report this, at least in the method section.

50 **Reply:** The sampling system size and weight are 50 cm × 50 cm × 50 cm (width × height × depth), and 4 kg except for a dewar (37 cm outer diameter, 66 cm height and 11 kg weight). For the field campaign, the system was disassembled. We carried the parts of the system in two containers 40 cm × 30 cm × 20 cm (width × height × depth) except for the dewar. Then,

we were able to assemble the sampling system on site and use the system. Therefore, we can carry our sampling system to field campaigns. We added this information to our manuscript.

Action: We added sampling system size and weight information and handles for the field campaign to our revised manuscript on 1st paragraph of section 2.2.

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Page 3, line 30 – Please explain the need for both glass-beads, Tenax TA, and Porapak N. On which of those is the OCS trapped? All of them?

Reply: We are sorry that we did not specify the necessity of each adsorbent in the sampling tubes. The sampling tube design is based upon the description by Bahlmann et al. (2011). According to Bahlman et al. (2011), glass beads trap the remaining water vapor from the sampled air and prevent adsorption of the water vapor on the Tenax TA and Porapak N and increase the temperature exchange between walls of the cryotrap and the sampled air. The Tenax TA and Porapak N can be used for trapping volatile organic compounds. We assume that OCS as our purpose is supposed to be sampled on the Tenax TA and/or Porapak N, but most of OCS might be trapped Tenax TA. Although some components might not be necessary for OCS collections, it works well for OCS sampling. Therefore, we do not plan to modify these in this system.

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Action: In the revised manuscript, we described the following on 2nd paragraph of section 2.2: “We developed this sampling tube according to Bahlmann et al. (2011). Detailed functions of respective components are described therein. Briefly, the glass bead traps the remaining water vapor from the sampled air and prevents water vapor adsorption on the Tenax TA and Porapak N. The glass bead further increases the temperature exchange between the cryotrap walls and the sampled air. The Tenax TA and Porapak N can be used for trapping volatile organic compounds. We assume that OCS is sampled on the Tenax TA and Porapak N, but most of OCS might be trapped on Tenax TA. Although some components might not be necessary for OCS collections, up to this point, it is working well for OCS sampling.”.

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Page 4, line 7 – “less than -110C”. Can you be more specific? It can be important for someone trying to use this method. Also, if you get as low as liquid N₂ temperature, than some O₂ (having higher boiling point) will be liquefied.

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Reply: We are sorry for the ambiguous sentence. Although it is difficult to keep the temperature constant using vapor of liquid N₂, we confirmed that the temperature in the dewar was at least -140 °C to -110 °C for 3 hr. Because the sampling tube temperature is over -140 °C, O₂ is not trapped in the sampling tube during sampling.

Action: We added the temperature during sampling 4th paragraph of section 2.2 (page 5 line 7) as follows: at temperatures of -140 to -110 °C.

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Page 6, line 5 – Rephrase. It should be explained in a different sentence that standard A is not pure OCS because of ...

Reply: Thank you for your comments.

Action: We separated the sentence in 1st paragraph of section 2.5 as follows: Reference OCS of sample A was purified with liquid N₂ (-196 °C) and then introduced via a conventional dual inlet system. Pure OCS is not commercially available in Japan because of its toxicity (Hattori et al. 2015).

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Page 7, line 11 – Refer to figure 3a.

Reply: Corrected accordingly.

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Page 7, line 23-24 – Not clear. Please rewrite.

Reply: We apologize for the unclear sentence.

Action: We rewrote the text to clarify the sentences (1st paragraph at section 3.2) 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.

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Page 8, Line 16. This is only true if the blanks always have atmospheric values. Please consider how it will affect the uncertainty in atmospheric measurements, if the blanks are in the expected range of OCS sources.

Reply: Thank you for your suggestion. We estimated the contamination effect for accuracy and precision of $\delta^{34}\text{S}(\text{OCS})$ values 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 ‰. The precision of our repeated measurement is ± 0.2 ‰. Then the overall precision of measurement is ± 0.4 ‰. Additionally, the standard deviation of four atmospheric samples we observed are ± 0.2 ‰. Therefore, the $\delta^{34}\text{S}(\text{OCS})$ value for atmospheric OCS at Suzukakedai campus was (10.5 ± 0.4) ‰. We modified precision and Figure 6 in our manuscript.

Action: We added some text to 2nd paragraph of section 3.2 as follows: **When considering (0.30 ± 0.16) nmol OCS (i.e. approx. 4 % for 8 nmol OCS samples) with $\delta^{34}\text{S}$ of 3–18 ‰ covering reported $\delta^{34}\text{S}$ range of OCS sources (Newman et al., 1990), the accuracy of the $\delta^{34}\text{S}(\text{OCS})$ can be shifted -0.3 to $+0.3$ ‰. Because the precision of 1σ uncertainty is 0.2 ‰, the overall precision values (1σ) for $\delta^{34}\text{S}$ of this sampling/purification system were estimated as 0.4 ‰. Additionally, we modified the error in Figure 6.**

Page 9, line 3 – The variability in concertation reported by Montzka (2007) is seasonal, not diurnal. Any possible explanation for the diurnal variability, and how it is related to what reported for other sites?

Reply: As you have pointed out, Montzka et al. (2007) did not observe diurnal variation of OCS concentration. For the diurnal variation of OCS concentration, we expected that the OCS concentrations are low at 12:00 compared to 00:00 because of plant uptake in our observation. However, we did not observe the trend. Berkelhammer et al. (2014) reported diurnal variation for OCS concentrations in USA with the lowest at 8:00 and the highest at 16:00 with 80 pmol mol^{-1} changes in a day. The differences of OCS concentrations for four atmospheric samples were smaller than 80 pmol mol^{-1} . The observed $\delta^{34}\text{S}(\text{OCS})$ values of four atmospheric samples were in the range of 10.4–10.7 ‰ (Figure 6b) and averaged (10.5 ± 0.4) ‰, and $\delta^{34}\text{S}(\text{OCS})$ values also showed no clear diurnal difference (p -value = 0.29) (Figure 6b). Given the diurnal OCS variations, future study is clearly necessary to test whether or not $\delta^{34}\text{S}(\text{OCS})$ values have diurnal variations by comparing $\delta^{34}\text{S}(\text{OCS})$ values for the highest OCS concentration at 8:00 and the lowest OCS concentration at 16:00. We added related discussion of the matter to the revised manuscript (3rd paragraph of section 3.3).

25 Reference

Berkelhammer, M., Asaf, D. Still, C., Montzka, S., Noone, D., Gupta, M., Provencal, R., Chen, H. and Yakir, D.: Constraining surface carbon fluxes using in situ measurements of carbonyl sulfide and carbon dioxide, *Global Biogeochem. Cycles*, 28, 161–179, 2014. doi:10.1002/2013GB004644.

30 Page 9, line 12 – Is this 1 permil change (not this small) is also accompanied by a change in concertation? Can this be related to the blank problem? Please explain in the text.

Reply: Yes, the 1 ‰ change might be caused by both isotopic fractionation for OCS decomposition and blank effect. When the contaminated OCS with $\delta^{34}\text{S}(\text{OCS})$ value of over 17 ‰ are considered, the $\delta^{34}\text{S}(\text{OCS})$ value can be increased by 1.2 ‰ in sample G. However, such a high $\delta^{34}\text{S}(\text{OCS})$ value in the blank is not reasonable because the contaminated OCS coming only from the ocean is not likely. Indeed, because the atmospheric $\delta^{34}\text{S}(\text{OCS})$ value observed in this study was 10.5 ‰, and OCS concentration in sample G was lower than atmospheric OCS concentration, the increased $\delta^{34}\text{S}(\text{OCS})$ value is expected to be affected by isotopic fractionation during OCS degradation in the cylinder.

Action: We added some text to the revised manuscript as follows: **It is possible to explain this 1.2 ‰ increase for $\delta^{34}\text{S}(\text{OCS})$ value for a case in which the contaminated OCS has $\delta^{34}\text{S}(\text{OCS})$ value with over 17 ‰. However, such a high $\delta^{34}\text{S}(\text{OCS})$ value from contamination requires a situation in which the contaminated OCS come only from the ocean, which is not likely. Because the atmospheric $\delta^{34}\text{S}(\text{OCS})$ values in this study were (10.5 ± 0.4) ‰ and higher than that for sample G, the increased $\delta^{34}\text{S}(\text{OCS})$ values are expected to be affected by isotopic fractionation during OCS degradation in the cylinder and not by contamination.**

45 Page 9, line 19 – What do you mean by “reasonable signals”

Reply: We apologize for the lack of clarity. We intended the words “reasonable signals” as a representative value when compared to $\delta^{34}\text{S}(\text{OCS})$ value of (4.9 ± 0.3) ‰ reported in Hattori et al. (2015) because the atmospheric $\delta^{34}\text{S}(\text{OCS})$ value of 10.5 ‰ is close to 11 ‰ as estimated based on the mass balance of OCS source from land and oceans. Additionally, because the OCS of compressed air in the cylinder can be decomposed and the $\delta^{34}\text{S}(\text{OCS})$ value may be changed in the cylinder, we

do not know if the OCS in the cylinder represents atmospheric OCS. If we consider the $\delta^{34}\text{S}(\text{OCS})$ value of 13‰ in Israel and Canary Islands reported by Angert et al. (2018) during process of review, the $\delta^{34}\text{S}(\text{OCS})$ values might not be homogeneous in the world.

Action: We deleted these words from our manuscript.

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Page 9, line 20 – “We earlier discussed”, where? In previous papers by the same group? I tried to read this in Hattori et al. (2015), but it is not clear to me. Please explain in more detail here how this isotopic balance was done. Also, if both the earlier value and the new value agree with the SSA value, then this is not a strong constraint for atmospheric OCS $\delta^{34}\text{S}$.

10 **Reply:** We are sorry for an inadequate explanation. First, “We earlier discussed” refers to the discussion described in Hattori et al. (2015) and by Leung et al. (2002). As you have pointed out, both $\delta^{34}\text{S}(\text{OCS})$ value of $(4.9 \pm 0.3) \text{‰}$ and $(10.5 \pm 0.4) \text{‰}$ agree with the $\delta^{34}\text{S}(\text{OCS})$ value of SSA value, indicating that it is not a strong constraint of $\delta^{34}\text{S}(\text{OCS})$ value for atmospheric OCS. However, we earlier hypothesized the $\delta^{34}\text{S}(\text{OCS})$ value of $(4.9 \pm 0.3) \text{‰}$ reported by Hattori et al. (2015) as a global signal, but it would be not correct. Therefore, we inferred the importance of showing that the new observed $\delta^{34}\text{S}(\text{OCS})$ value is suitable as a sulfur source of SSA, but it is still similar to a discussion put forth by Schmidt et al. (2013), who
15 hypothesized a $\delta^{34}\text{S}(\text{OCS})$ value of 11 ‰ according to Newman et al. (1990). Because the discussion has already been reported and because the $\delta^{34}\text{S}(\text{OCS})$ value is close to 11 ‰, we deleted these discussions and instead used a more detailed description in the revised manuscript.

Action: We delete these discussions in favor of more detailed description in the revised manuscript.

20 Page 10, Line 3 – Please report the magnitude of these effects, and estimate how this should influence the atmospheric OCS.

Reply: First, sulfur isotopic fractionations of OCS for the troposphere was estimated as -5 to 0‰ for reaction with OH radical (Schmidt et al., 2012), -2 to -4‰ for decomposition by soil microorganisms (Kamezaki et al., 2016; Ogawa et al., 2017) and -5.3‰ for plant uptake (Angert et al., 2018). We added these values to our manuscript. We added Angert et al. (2018) as a new reference.

25 Secondly, we discussed how isotopic fractionation influences $\delta^{34}\text{S}(\text{OCS})$ values for atmospheric OCS as follows: all isotopic fractionation constants by OCS degradation are negative, indicating that the $\delta^{34}\text{S}(\text{OCS})$ values can be increased by OCS degradation in the troposphere. Because the main OCS sink is photosynthesis by plants, the $\delta^{34}\text{S}(\text{OCS})$ values in the atmosphere might be increased during the growing season in April. However, because of the long lifetime of OCS, the changes in $\delta^{34}\text{S}(\text{OCS})$ values might not be detected with a seasonal pattern. Future studies must be conducted for
30 determination of isotopic fractionation constant and observation of $\delta^{34}\text{S}(\text{OCS})$ values to estimate the dynamics of atmospheric $\delta^{34}\text{S}(\text{OCS})$ values in troposphere.

Action: We added isotopic fractionation constants for OCS degradation process in our revised manuscript and discussed the matter in the revised manuscript (1st and 2nd paragraph at section 3.5).

References:

35 Angert, A., Said-Ahmad, W., Davidson, C., and Amrani A.: Sulfur isotopes ratio of atmospheric carbonyl sulfide constrains its sources, Scientific Reports, 9(741), 1-8, 2018.

Page 10, line 29 – These “further investigations” seem critical to establish the method. Are there new results since the manuscript was first submitted?

40 **Reply:** Yes, we conducted further OCS preservation testing and added the results to section 3.4 in the revised manuscript. We added the results as follows: A rapid OCS decomposition of approximately 20 % during 7 days of storage was observed for the stainless steel adsorption tubes stored at 25 °C. A similar pronounced loss was observed for the Sulfinert-treated adsorption tubes stored at 4 °C but at a storage temperature of -20 °C . The OCS was stable for 30 days at -20 °C , and for at least 90 days at -80 °C within 1σ uncertainty of 6 % (Figure 8a). Furthermore, we found that the $\delta^{34}\text{S}(\text{OCS})$ values showed
45 no significant change during storage for at least 14 days at -80 °C (Figure 8b). These results demonstrate that it is possible to apply this method for field campaigns by storing the adsorption tube at -80 °C after sampling.

Page 11, line 26 – Please be more specific. Instead of “some shortcomings in terms of sample amount” write down the ratio of sample amounts in the two methods.

Reply: We apologize for an ambiguous sentence.

Action: We added “**IR-MS method requires a 300 times larger sample OCS than GC/MC-ICP-MS method.**” to section 3.6.

5 Page 11 - The conclusion section mentions for the first time another method (by Said-Ahmad, 2017). The mentioning of other existing methods should be done in the introduction, and comparison with other methods should be in the discussion, and include advantages and disadvantages. Similarly, writing in the last lines of the paper that the current method has the advantage of enabling carbon and oxygen isotopes measurements seems out of place, since this is not demonstrated in the current manuscript. However, this can be mentioned in the discussion.

Reply: We agree with your suggestion.

10 **Action:** We added the GC/MC-ICP-MS method to the *Introduction* section. We made section 3.6 to present a comparison between IR-MS method and MC-ICP-MS method. Although our IR-MS method has shortcomings related to the sample size, we emphasize that this IRMS method can potentially be updated to multiple isotope measurement with carbon and oxygen isotopes. Also, we deleted the discussion related to carbon and oxygen isotope of OCS from the *Conclusion* section.

15 The discussion should also refer to the new paper by Angert et al., mentioned in the online discussion. Are the atmospheric values reported by the two papers identical, considering all experimental uncertainties? If not, is this a methods issue, or a real geographic effect?

20 **Reply:** As you have recommended, we cited Angert et al. (2018) in the revised manuscript. The $\delta^{34}\text{S}(\text{OCS})$ values of 13 ‰ reported by them are not the same as ours. Because our data are calibrated with the IAEA standard with to obtain δ value with VCDT scale via chemical conversion from OCS to SF_6 , we do not expect that a 3 ‰ difference originates from some method-related difficulties in our system. To clarify whether or not we have method-related problems, inter-laboratory calibration is expected to be helpful for future studies.

25 Additionally, the geographic effect might induce differences of the $\delta^{34}\text{S}(\text{OCS})$ value between the two studies. In the revised manuscript, we discussed geographic effects that can be considered for explanation of the variations in $\delta^{34}\text{S}(\text{OCS})$ values. To discuss geographic effects, we added this discussion at 4th paragraph in section 3.5 and added a new citation as a relevant reference: Zumkehr et al. (2018).

Reference

30 Zumkehr, A., Hilton, T. W., Whelan, M., Smith, S., Kuai, L., Worden, J., Campbell, J. E.: Global gridded anthropogenic emissions inventory of carbonyl sulfide, *Atmos. Environ.*, 183, 11-19, 2018.

Figure 3a – Maybe better to show versus sampling time (and not run number). Also the 10min is black in the legend and gray in the figure.

35 **Reply:** Thank you for your suggestion. We believe that the combination of Figure 3a and 3b nicely presents that there was no memory effect, and the relation between sampling time and OCS amount collected. Therefore, we retain this in the revised manuscript, but we changed the legend color from black to gray in the legend of Figure 3.

Action: We changed the legend color from black to gray in the legend of Figure 3.

Figure 8 – Better to start the y-axis at 80%. Also, need to show longer preservation periods.

40 **Reply:** Thank you for your suggestion. We did not start at 80 % on the y-axis because we added the OCS preservation results. We added results of longer preservation tests of OCS storage in adsorption tubes.

Thank you for reviewing our manuscript.

45 Shohei Hattori on behalf of co-authors.

Blue: Referee comments

Black: Our comments

Red: The sentences in our manuscript

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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-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.

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Reply: Thank you for reviewing our manuscript and for recognizing the importance of this study. We believe that the investigation of isotopic composition for carbonyl sulfide (OCS) can improve understanding of sulfur and carbon cycle.

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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 ~10nmol of COS, in the case of the present study). Secondly, COS is an extremely reactive gas that can be hydrolyzed and/or produced rapidly from many surfaces and materials commonly used in gas exchange techniques.

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Reply: As you have pointed out, collection of OCS from air and potential interface from preservation/loss of OCS during sampling are important for isotope analysis of OCS. For this study, we specifically examined how to collect OCS from air. We verified OCS contamination and OCS loss during measurement. This study is expected to be useful for situations in which large amounts of OCS, such as measurement of carbon and oxygen isotopic ratios of OCS, are required in the future, as we have described in our manuscript.

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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 -110oC. This could be a bit more specific as pointed out by one of the reviewers as other gases may condense at lower temperatures.

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Reply: We are sorry for the ambiguous sentence. Although it is difficult to keep the temperature constant using vapor of liquid N₂, we confirmed that the temperature in the dewar was -140 °C to -110 °C for at least 3 h. Because the sampling tube temperature was higher than -140 °C, O₂ is not trapped in the sampling tube during sampling. We increased the temperature during sampling.

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Action: We added an explanation of the temperature range of the sampling tube to our revised manuscript.

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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 12H before sampling and require high temperatures starting at 160oC and reaching 330oC 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 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?

Reply: We recognize that OCS contamination can be a serious issue. Indeed, although Tenax TA is suitable for OCS collection because of high-temperature conditioning, several picomoles of OCS are always observed from Tenax TA as blank. As you have pointed out, to reduce OCS blank from adsorbent as much as possible, we conditioned sampling and adsorption tubes for 6 h using pure helium (99.99995 % purity). The conditioning of sampling and adsorption tubes can be prepared in the laboratory before the field observation. We confirmed that the surface was inert for at least three days and the inactive state of the surface of adsorbents in these tubes would be retained under a no leakage condition. However, at present, we recommend conditioning immediately before use to the greatest degree possible. Note that the conditioning steps would be required if stainless tubes are replaced by Sulfinert-treated tubes/valves, because the aim of conditioning is to include removal of strongly adsorbed volatile organic compounds such as ethanol and acetaldehyde in adsorbents. Given that these stored in the adsorption tube might block OCS collection and react with OCS (Ferm, 1957), we must remove these compounds as much as possible.

Finally, the time span is the following: sampling for 100 min (500 L), transfer for 40 min, pre-concentration for 40 min, and measurement using Q-MS or IR-MS for 20 min.

Action: We added information related to conditioning to section 3.3.

[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?](#)

Reply: As you have understood, we did not use Sulfinert-treated adsorption tubes for most of the experiments. As we added to Figure 8 in the revised manuscript, the OCS amount in a stainless steel adsorption tube stored at room temperature preserved (-6 ± 6 %) of OCS, with no significant changes in $\delta^{34}\text{S}(\text{OCS})$ values within (0.2 ± 0.4 %) after 3 h. All data sets are measurements taken right after the sampling (i.e. shorter than 30 min.). Therefore, we did not expect significant changes in OCS concentrations and the $\delta^{34}\text{S}(\text{OCS})$ values.

Action: We added this information in the revised manuscript in section 3.4.

[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 \(e.g. \$G = 160 \text{ pmol mol}^{-1}\$ \), 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?](#)

Reply: We are sorry that these ambiguous sentences have led to confusion. We found that there are three questions in this comment. First is for the material of cylinder. Second is for how to ensure OCS concentration if the OCS decomposed in cylinder. Third is for trends of OCS decomposition in the cylinder.

First, all cylinders are made of manganese steel without special wall treatments to minimize contamination.

Secondly, as you have expressed, the OCS concentrations and sulfur isotopic compositions for OCS can be changed in some cylinders. This is also a reason why we developed this method. To estimate OCS concentration, the OCS concentrations for sample A and sample B were calibrated using diluted in-house synthesized OCS (i.e. 100 %) to 10 % by high-purity He using a vacuum line. We confirmed that the OCS concentration and isotopic composition for sample B had not changed for four years after we published Hattori et al. (2015). Therefore, the calibration curved was made by using sample B and sample B was used as the daily working standard for sulfur isotopic measurement. The OCS samples in

5 compressed air in the cylinder, on the other hand, were not stable: we found that the OCS concentration in sample H was decomposed to one third within three months. For that reason, we must conduct experiments immediately after we determined OCS concentrations. Therefore, for the example to make Figure 3, OCS in sample F were collected within two days to evaluate collection efficiency, followed by the determined OCS concentration in sample F within a week by calibration with sample B. In a similar manner, the cylinders of sample H, I, J, and K were used for experiment within 2–3 days. Therefore, we do not expect the changes in OCS concentration during the experimental period. Indeed, the effect OCS decomposition was not shown in Figure 3 or Figure 8a. We again emphasize, as you have stated, that the OCS contamination and its sulfur isotopic composition is not likely to be preserved in the cylinder. Also, no scrubber is used when the compressed air was filled in the cylinder.

10 Thirdly, the OCS concentration in sample B is monitored every time before the experiment. However, we do not monitor the OCS concentration of compressed air in cylinder because we know that the OCS do not preserve the $\delta^{34}\text{S}(\text{OCS})$ value. As you suggest, we will plan to use a Sulfinert-treated cylinder and ACULIFE for the standard sample. Thank you for informing us.

To the revised manuscript, we added the following information in section 2.1 and 2.4:

- 15 • Cylinder Material: “manganese steel without special wall treatments” .
• Time span for measurement for sample F, H, I, J and K .
• How we determined OCS concentration in sample A and B: “ The OCS concentrations for samples A and B were determined against to the in-house synthesized OCS (i.e. 100 %) diluted to 10 % using high-purity He (99.99995 % purity; Japan Fine Products Co. Ltd.). It is noteworthy that the OCS concentration in sample B had showed no change at least four years after the publication of Hattori et al. (2015).”
- 20

I also think it would be worth discussing a little the caveats surrounding the fragmentation IRMS approach for example the potential for O_2 contamination and consequences for the $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ analysis/interpretation.

25 **Reply:** Thank you for your suggestion. However, the caveats of fragmentation IRMS have already been discussed by Hattori et al. (2015). To avoid duplication, we did not add that information to the revised manuscript. As we described in that earlier report by Hattori et al. (2015), the influence by O_2 contamination to $\delta^{34}\text{S}(\text{OCS})$ value was also discussed; the $\delta^{34}\text{S}$ value are increased with the OCS amount depleted. The trend can be caused not by O_2 contamination because of natural abundance of rare oxygen isotope (see Hattori et al. (2015) for more detail). Although we must consider isotopic fractionation in ion source in IRMS and its sample size dependency, the effects of size dependence are negligible over 6 nmol of OCS in this study. We added points raised here.

30

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.

Reply: We agree with your suggestion. We moved the results of preservation to section 3.4.

35 I also feel that the first paragraph of the conclusion is repetition of the results and should be removed.

Reply: Thank you for your suggestion. However, the summary of results is important for this method paper. For that reason, we changed the section title from “*Conclusion*” to “*Summary*”.

40 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.

Reply: Agreed. We moved the discussion of carbon and oxygen to the *Discussion*.

Other details

45 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.

Reply: We checked all parentheses. We corrected parentheses as much as we can.

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.

5 **Reply:** As you have noticed, the both $\delta^{34}\text{S}(\text{OCS})$ value are in the range of expected $\delta^{34}\text{S}(\text{OCS})$ source. However, $\delta^{34}\text{S}(\text{OCS})$ value of 4.9 ‰ for compressed air in cylinder might be affected by decomposition in the cylinder and contamination from the compressor. However, $\delta^{34}\text{S}(\text{OCS})$ value of 10.5 ‰ is collected atmospheric OCS directly. To clarify this point, we added the “previous values of $\delta^{34}\text{S}(\text{OCS}) = (4.9 \pm 0.3)$ ‰ of compressed air in the cylinders were not representative samples for a global signal.” to the revised text.

Page 2 Line 8 remove “net ecosystem exchange into” from this sentence.

10 **Reply:** Corrected accordingly.

Page 3 Line 11 state the purity of the Helium in %

Reply: We added the text “99.99995 % purity” to the revised manuscript.

Page 3 Line 12 can you provide more details of the exact S compounds used

15 **Reply:** We apologize for the ambiguous information. We used commercial sulfur powders. We added information related to sulfur powders and purity in our manuscript.

Page 3 Line 16 what type of commercial cylinders provide details and how often they were measured.

20 **Reply:** We used manganese steel cylinders without special wall treatment. The OCS concentration in sample A were measured every month. The OCS concentrations in sample B were measured before every experiment. Other OCS concentrations of compressed air in the cylinder were measured once except for the preservation test.

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?

25 **Reply:** We added information related to the compressor in section 2.1. The filter was not used for filling compressed air in a cylinder. The compressed air was not dried.

Page 3 Line 20 this is a super vague statement can you provide details of how you checked for stability.

30 **Reply:** We are sorry for including this unclear sentence. We deleted the sentence from the revised text because of duplication. Moreover, the method for preservation test was described in section 3.4.

Page 4 Line 3-4 can you explain how the heating was made and where was this step made in the lab or outside?

Reply: We conditioned using heating mantles in the laboratory.

35 **Action:** We added information to 3rd paragraph of section 2.2.

Page 4 Line 15 removed using what?

Reply: We removed the sampling tube from liquid nitrogen by hand.

Action: We added “manually” to this sentence (5th paragraph of section 2.2).

40 Page 4 Line 27-28 is the tubing flexible i.e. in a coil or rigid?

Reply: The tubes are made of stainless steel, but we can bend them.

Action: We added the U-shaped or coil-shaped before the trap.

Page 4 line 29 how is the heating achieved?

45 **Reply:** We used heating mantles for heating trap 2.

Action: We added information about the heater to 1st paragraph of section 2.3.

Page 4 line 30 why use steel and not glass. I guess this was later switched to a sulfinert tube?

Reply: There are three reasons for using stainless steel for traps. Glass also adsorbs OCS, stainless steel is easy to handle compared to glass. Also, the stainless steel has higher thermal conductivity than glass. We will change stainless steel tubes to Sulfinert-treated tubes in future work.

5 Page 5 line 8 this should be -72°C

Reply: Corrected accordingly.

Page 5 Line 11 where did this injected gas come from?

Reply: We are sorry for the lack of information.

10 **Action:** We modified the sentence as follows: **The retention times of CO₂ and OCS were initially determined by injecting a mixture of 8 mmol of CO₂ from pure CO₂ in a cylinder (99.995 % purity; Japan Fine Products Co. Ltd.) and 10 nmol of OCS from sample C in 2nd paragraph of section 2.3.**

Page 5 lines 22-25 not written very clearly please improve

15 **Reply:** We apologize for this unclear sentence. We think that it is difficult to understand why we made two kinds of calibration curves and how we made calibration curves.

Action: We rewrote the information in 2nd and 3rd paragraph of section 2.4.

Page 5 line 25 how many replicates were analysed to obtain the precision?

20 **Reply:** We injected sample B in triplicate for each amount of sample size. The precisions were estimated by standard deviation of relative error between measured values and values estimated from calibration curves. The obtained precision was $\pm 3\%$.

25 **Action:** We added “ $n = 3$ ” and “**The precision (standard deviation (1σ) relative to mean) of the OCS amount by a syringe injection was estimated $\pm 3\%$ by the standard deviation of the relative error between the measured values and the estimated value for calibration curves.**” in 2nd paragraph of section 2.4.

Page 6 line 11 size of capillary tube?

Reply: We added capillary tube size information here.

30 Page 6 line 9 spec of the diaphragm pump type, flow, pressure?

Reply: We used a rotary pump (Pascal 2010; Pfeiffer Vacuum GmbH, Aßlar, Germany). Although we do not know the flow rate and pressure of pumping, we evacuated He gas at approximately 0.3 kPa per second from 30 cm³ by regulating the seal valve (SS-4TW; Swagelok Co., Ohio, USA).

35 **Action:** We added the following to our manuscript: **by a rotary pump (Pascal 2010; Pfeiffer Vacuum GmbH, Aßlar, Germany) gently with regulation using a valve.**

Page 6 line 16 tank ID please

Reply: The tank is sample B. We added the information to this sentence.

40 Page 7 line 18-20 this sentence does not make sense to me

Reply: We apologize for the unclear text. We thought that it would be difficult to identify the OCS blank.

Action: We changed “OCS blank” to “OCS contamination”.

Page 7 line 21-22 ambiguous sentence

45 **Reply:** We apologize for the unclear sentence.

Action: We rephrased the text to the following: **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.

Page 7 line 26 how? And what does slowly mean?

5 **Reply:** We conducted the experiment manually. We changed slowly into “over 30 min by syringe” in this part.

Action: We added “manually” and “over 30 min by syringe” in our manuscript.

Page 8 line 15 could you explain these OCS blanks please

10 **Reply:** We used the OCS blank as OCS contamination. Therefore, we changed “OCS blank” into “OCS contamination”

Page 9 line 11 check the units here please and correct

Reply: We are sorry for mistakes in the use of units. We changed the “500 nmol mol⁻¹” to “500 pmol mol⁻¹”.

Page 9 line 14 hydrolysis requires water were your tanks dry?

15 **Reply:** The compressed air in the cylinder is collected just as air collected by the compressor. For that reason, the air was not dried. Additionally, Kamezaki et al. (2016) reported not hydrolysis but abiotic OCS decomposition.

Action: We deleted “OCS is decomposed by hydrolysis, which increases the $\delta^{34}\text{S}(\text{OCS})$ value.” from our revised manuscript.

Page 9 line 28-30 this sentence needs rewritten as it does not make sense to me

20 **Reply:** We apologize for the unclear sentence. We thought that we did not show the proportion to what.

Action: We changed the sentence in 1st paragraph of section 3.5 as follows: **The $\delta^{34}\text{S}(\text{OCS})$ value of $(10.5 \pm 0.4) \text{‰}$ is generally consistent with earlier estimation by Newman et al. (1991), which expected the $\delta^{34}\text{S}(\text{OCS})$ values based on the flux of proportional to the organic matter were produced by photosynthesis as 3 ‰ and oceanic emission as 18 ‰ (Newman et al., 1991).**

Page 10 generally there is little statistical testing reported in this paper in general

25 **Reply:** Thank you for the comment. For statistical analyses, we used *p*-tests. We assumed that the averaged OCS concentrations and $\delta^{34}\text{S}(\text{OCS})$ values in day and night are not significantly different. The calculated *p*-values are 0.65 and 0.29, for OCS concentrations and $\delta^{34}\text{S}(\text{OCS})$ value, respectively. These values are over 0.05. Therefore, significant differences are not observed for OCS concentrations and $\delta^{34}\text{S}(\text{OCS})$ values of day and night. To the revised manuscript, we added *p*-values.

Page 10 this section would really benefit from more results using the sulfinert equipment.

30 **Reply:** We added all data accumulated from now to Figure 8 in section 3.4.

35 Thank you for reviewing our manuscript.

40 Shohei Hattori on behalf of the authors.

Reply to RC3 from Referee #1

Blue: Referee comment

Black: Our comment

5 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.

10 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.

15 **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.

20 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.

25 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.

30 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?

35 **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.

40 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 : $\delta^{34}\text{S} = -0.30\text{‰}$; 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 $(14.1 \pm 0.2)\text{‰}$ in this study, showing no significant difference with the $\delta^{34}\text{S}(\text{OCS})$ value of sample B $(14.3 \pm 0.2)\text{‰}$ 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.

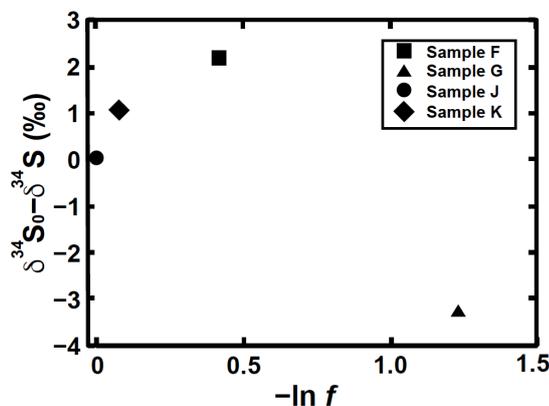


Figure R1: Relative $\delta^{34}\text{S}(\text{OCS})$ value relative to the natural logarithm of the residual OCS fraction. We assumed sample J have original OCS concentration and $\delta^{34}\text{S}(\text{OCS})$ value.

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 ± 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: $\text{O}(^3\text{P})$ – 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.

5

- 8/26 to 8/28: Remove colon (:) after m/z (e.g. m/z 32)

Reply: Removed all colons (:) with m/z .

10

- 9/5: USA

Reply: Corrected accordingly.

- 11/5: proofed -> showed

Reply: Corrected accordingly.

15

Thank you for reviewing our manuscript.

Shohei Hattori on behalf of co-authors.

(marked-up manuscript)

Large volume air sample system for measuring $^{34}\text{S}/^{32}\text{S}$ isotope ratio of carbonyl sulfide

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10

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Abstract

Knowledge related to sulfur isotope ratios of carbonyl sulfide (OCS or COS), the most abundant atmospheric sulfur species, remains scarce. Earlier method developed for sulfur isotopic analysis for OCS using S^+ fragmentation by isotope ratio mass spectrometer is inapplicable for ambient air samples because of the large samples required (approx. 500 L of 500 pmol mol⁻¹ OCS). To overcome this difficulty, herein we present a new sampling system for collecting approx. 10 nmol of OCS from ambient air coupled with a purification system. Salient system features are (i) accommodation of samples up to 500 L (= approx. 10 nmol) of air at 5 L min⁻¹, (ii) portability of adsorption tubes (1/4 inch (0.64 cm) outer diameter, 17.5 cm length, approx. 1.4 cm³ volume) for preserving the OCS amount and $\delta^{34}\text{S}(\text{OCS})$ values at $-80\text{ }^\circ\text{C}$, respectively, for up to 90 days and 14 days, and (iii) purification OCS from other compounds such as CO_2 . We tested the OCS collection efficiency of the systems and sulfur isotopic fractionation during sampling. Results show precision (1σ) of $\delta^{34}\text{S}(\text{OCS})$ value as 0.4 ‰ for overall procedures during measurements for atmospheric samples. Additionally, this report presents diurnal variation of $\delta^{34}\text{S}(\text{OCS})$ values collected from ambient air at Suzukakedai campus of Tokyo Institute of Technology located in Yokohama, Japan. The observed OCS concentrations and $\delta^{34}\text{S}(\text{OCS})$ values were, respectively, 447–520 pmol mol⁻¹ and from 10.4 ‰ to 10.7 ‰ with a lack of diurnal variation. The observed $\delta^{34}\text{S}(\text{OCS})$ values in ambient air differed greatly from previously reported values of $\delta^{34}\text{S}(\text{OCS}) = (4.9 \pm 0.3)\text{ }^\circ\text{‰}$ for compressed air collected at Kawasaki, Japan, presumably because of degradation of OCS in cylinders and collection processes for that sample. Consequently, previous values of $\delta^{34}\text{S}(\text{OCS}) = (4.9 \pm 0.3)\text{ }^\circ\text{‰}$ of compressed air in the cylinders were not representative samples for a global signal. Based on the field samples analyzed in this study, we instead propose of a $\delta^{34}\text{S}(\text{OCS})$ value of $(10.5 \pm 0.3)\text{ }^\circ\text{‰}$ for the tropospheric OCS. The system presented herein is useful for application of $\delta^{34}\text{S}(\text{OCS})$ for investigation of OCS sources and sinks in the troposphere to elucidate its cycle.

30

1 Introduction

Carbonyl sulfide (OCS) is the most abundant sulfur-containing gas in ambient air with atmospheric concentrations of approx. 500 pmol mol⁻¹ in the troposphere (Chin and Davis, 1995; Montzka et al., 2007). In fact, OCS can be transported to the stratosphere because the average residence time of OCS is longer than two years (Brühl et al., 2012). In the stratosphere, it is converted to stratospheric sulfate aerosols (SSA) through atmospheric sink reactions (Crutzen, 1976). Therefore, OCS must be regarded as an important sulfur source for SSA, playing an important role in the Earth's radiation budget and in ozone depletion. Moreover, because leaves consume OCS whenever assimilating CO₂, but do not emit OCS to the atmosphere by respiration (Sandvalo-Soto et al., 2005), OCS can be a tracer of gross primary production (GPP) on land (Campbell et al., 2008). For those reasons, elucidating the OCS dynamics in the atmosphere is important to elucidate the carbon cycle. Nevertheless, tropospheric OCS sources and sinks entail great uncertainty (Watts, 2000; Kremser et al., 2016) because of missing sources in the atmospheric budget of 230–800 Gg a⁻¹ S equivalents as revealed by top-down modelling (Berry et al., 2013; Glatthor et al., 2015; Kuai et al., 2015).

Isotope analysis is a useful tool to trace sources and transformations of trace gases (Johnson et al., 2002; Brenninkmeijer, 2003). To quantify OCS sources and sinks in natural environments using isotope analysis, determination of isotopic fractionation for reactions and ambient measurements is required. To date, isotopic fractionations occurring in the reactions of OCS have been determined for almost all OCS sink reactions in the stratosphere: OCS photolysis (Hattori et al., 2011; Lin et al., 2011; Schmidt et al., 2013) as well as reactions with OH (Schmidt et al., 2012) and O(³P) (Hattori et al., 2012). Furthermore, the sulfur isotopic fractionation during soil bacterial degradation and enzymatic degradation were ascertained based on laboratory experiments (Kamezaki et al., 2016; Ogawa et al., 2017). Based on the analysis of commercially available compressed air our group suggested a $\delta^{34}\text{S}$ value of $(4.9 \pm 0.3) \%$ for tropospheric OCS (Hattori et al., 2015). However, very recently, Angert et al. (2018) reported a markedly different $\delta^{34}\text{S}$ value of $(13.1 \pm 0.7) \%$ for tropospheric OCS using a gas chromatograph (GC)/multi collector-inductively coupled plasma mass spectrometer (MC-ICP-MS). For the measurement of sulfur isotope ratios ($\delta^{33}\text{S}$, $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values) of OCS in our laboratory, an online method measuring on a GC/isotope ratio (IR)-MS using S⁺ fragmentation ions had been developed (Hattori et al., 2015). This method supports simple analysis of sulfur isotopic compositions of OCS over 8 nmol. However, application this method for atmospheric samples has yet to be done by this GC/IR-MS method, because of the large sample amounts that are necessary (i.e. 500 L of 500 pmol mol⁻¹ OCS). Therefore, we aimed to develop a large volume air sampling system to apply S⁺ IR-MS method for atmospheric samples.

To date, several methods have been developed for concentration measurements using grab samples of air coupled with sampling/purification systems in the laboratory (e.g. Inomata et al., 1999; Xu et al., 2001; Montzka et al., 2004; Kato et al., 2012). Most systems collect 2–5 L of atmospheric samples for measuring OCS concentrations. The collected OCS is extracted in the laboratory with a combination of adsorbents at subambient temperatures: Tenax TA with dry ice/methanol (Inomata et al., 1999) or dry ice/ethanol (Hattori et al., 2015), glass beads with liquid oxygen (Montzka et al., 2004) or liquid

argon (Xu et al., 2001), 2,3-Tris (2-cyanoethoxy) propane with liquid oxygen (Kato et al., 2012). Grab sampling, however, is unrealistic when collecting 500 L of air. Therefore, we developed a large-volume air sampling system for measuring sulfur isotope ratios of OCS. We modified a large-volume air sampling system developed for carbon isotope measurement for halocarbons such as chloromethane and bromomethane, which have concentrations of pmol mol⁻¹ level in ambient air (Bahlmann et al., 2011). Subsequently, we combined this sampling system and newly developed an online OCS purification system for separation from impurities such as CO₂, which is 10⁶ times more abundant in air than OCS. For the current study, we describe the systems and its applications to atmospheric observation. We provide first results for diurnal variations of δ³⁴S(OCS) in ambient air from samples collected at Suzukakedai campus of the Tokyo Institute of Technology located in Yokohama, Japan.

2 Materials and methods

2.1 Samples

An overview of the synthetic samples used for method evaluation in this study is given in Table 1. Commercial samples containing 10.5 % OCS balanced with high-purity He as sample A (99.99995 % purity; Japan Fine Products Co. Ltd., Kawasaki, Japan) and 5.9 μmol mol⁻¹ OCS balanced with high-purity He as sample B (99.99995 % purity; Japan Fine Products Co. Ltd.) were used (Table 1). Furthermore, we synthesized OCS from three kinds of sulfur powders, designated as sample C produced from sulfur power (99.99 % purity; Fujifilm Wako Pure Chemical Corp., Japan), sample D produced from sulfur powder (99.98% purity; Sigma-Aldrich Corp. LLC, Missouri, USA), and sample E (a mixture of sulfur powders used for samples C and D) with a reaction with CO (99.99 % purity; Japan Fine Products Co. Ltd., Kawasaki, Japan) in a similar manner to that described by Ferm (1954) and Hattori et al. (2015) (Table 1). The OCS concentrations for samples A and B were determined against to the in-house synthesized OCS (i.e. 100 %) diluted to 10 % using high-purity He (99.99995 % purity; Japan Fine Products Co. Ltd.). It is noteworthy that the OCS concentration in sample B had showed no change at least four years after the publication of Hattori et al. (2015).

For the testing of repeatability and collection efficiency of the systems, we used three commercially available cylinders of compressed air samples in a collected in Kawasaki, Japan (Toho Sanso Kogyo Co., Ltd., Yokohama, Japan), sample F (collected on 25 July 2017), sample G (collected on 2 July 2012), sample H (collected on 2 December 2017), sample I (collected on 26 October 2018), sample J (collected on 1 December 2018), and sample K (collected on 26 December 2018) (Table 2). These compressed air samples in these cylinders are collected by compressor (YS85-V; Toa Diving Apparatus Co., Ltd., Tokyo, Japan) and are not dried. Sample G was used as sample E for Hattori et al. (2015). Its δ³⁴S(OCS) value was (4.9 ± 0.3) ‰. It was postulated as the global representative value at that moment. All compressed air cylinders are made of manganese steel without special wall treatments, engendering concerns about OCS decomposition in the cylinders.

2.2 Sampling system

A schematic diagram of the sampling system is depicted in Figure 1. The sampling system size and weight are 50 cm × 50 cm × 50 cm (width × height × depth), and 4 kg except for a dewar (37 cm outer diameter, 66 cm height and 11 kg weight) (MVE SC 20/20; Chart Industries Inc., Georgia, USA). For field campaigns, the system can be easily disassembled and transported in two containers of 40 cm × 30 cm × 20 cm (width × height × depth). Reassembling the sampling system on site can easily be done within 2 h making it suitable for field campaigns. Main compartments of the sampling system are 1/4 inch (0.64 cm) PTFE tubes, 1/8 inch (0.32 cm) stainless steel tubes, 1/16 inch (0.16 cm) Sulfinert-treated stainless steel tubes (Restek Corp., PA, USA), Sulfinert-treated stainless steel ball valves V1, V2, V5, and V9, and stainless steel ball valves V3, V4, V6, V7, and V8 behind the sampling tube (Figure 1). Excluding union tees made of stainless steel immediately before the pump, union tees coming in contact with the sampled OCS are made of Sulfinert-treated stainless steel (Figure 1).

The cryotrap sampling tube for OCS concentration from ambient air consists of an outer stainless steel tube (3/4 inch (1.9 cm) outer diameter, 50 cm length) with an air inlet at the side 4 cm below the top and an inner 1/4 inch (0.63 cm) stainless steel tube (Bahlmann et al., 2011). From top to bottom, the sampling tube package is the following: 0–30 cm, empty; 30–40 cm, silanized glass beads 2 mm; 40–43 cm, Tenax TA (60/80 mesh; GL Science Inc., Tokyo, Japan); 43–47 cm, Porapak N (80/100 mesh; Sigma-Aldrich Corp., Japan); 47–50 cm, empty, and adsorbents separated by plugs of precleaned glass wools (GL Science Inc., Tokyo, Japan). We developed this sampling tube according to Bahlmann et al. (2011). Detailed functions of respective components are described therein. Briefly, the glass bead traps the remaining water vapor from the sampled air and prevents water vapor adsorption on the Tenax TA and Porapak N. The glass bead further increases the temperature exchange between the cryotrap walls and the sampled air. The Tenax TA and Porapak N can be used for trapping volatile organic compounds. We assume that OCS is sampled on the Tenax TA and Porapak N, but most of OCS might be trapped on Tenax TA. Although some components might not be necessary for OCS collections, up to this point, it is working well for OCS sampling.

The adsorption tube consists of a stainless steel tube (with 1/4 inch (0.63 cm) outer diameter, 17.5 cm length) filled with Tenax TA. Before experiments, the sampling tube and the adsorption tube were conditioned in the laboratory, respectively, using 100 mL min⁻¹ high-purity He flow at 160 °C with an electric heating mantle (P-22; Tokyo Technological Labo Co., Ltd., Kanagawa, Japan) for 6 h and 50 mL min⁻¹ high-purity He flow at 330 °C by an electric heating mantle (P-25; Tokyo Technological Labo Co., Ltd.) for 6 h. We confirmed that possible contamination of OCS in the tubes was less than 10 pmol after conditioning. We also confirmed that the surface was inert at least three days and that the inactive state of the surface of adsorbents in these tubes would be maintained under a no-leakage condition. It is noteworthy that conditioning steps would be required if stainless tubes are replaced by Sulfinert-treated tubes/valves because this conditioning was aimed at removing strongly adsorbed volatile organic compounds such as ethanol and acetaldehyde in adsorbents, which might interfere with OCS collection and/or react with OCS.

During sampling, the valves V1, V2, V3 and V4 were opened. Then atmospheric samples were drawn with a low volume diaphragm pump (LV-40BW; Sibata Scientific Technology Ltd., Saitama, Japan) through the sampling system with flow of (5.00 ± 0.25) L min^{-1} . The air was first passed through a membrane filter (47 mm diameter, 1.2 μm pore, Pall Ultipor N66 sterilizing-grade filter; Pall Corp., New York, USA) set in a NILU filter holder system (70 mm diameter, 90 mm length; Tokyo Dylec Corp., Tokyo, Japan) to remove atmospheric aerosol. Then it was directed through a condenser (EFG5-10; IAC Co. Ltd., Japan) kept at approximately -15 $^{\circ}\text{C}$ to remove water vapor from the air. The air was then passed through the sampling tube at temperatures of -140 to -110 $^{\circ}\text{C}$ by vapor of the liquid N_2 in a dewar. The OCS was enriched in the sampling tube, whereas other main gases (N_2 , O_2 , Ar, etc.) were passed through the sampling tube.

After sampling, the valves V1 and V4 were closed; and the valves V5, V6, V7, and V8 were opened. Then, the sampling tube was removed carefully from the dewar manually and was heated gradually to 130 $^{\circ}\text{C}$. The vaporized gases in the sampling tube were passed to the adsorption tube cooled at -78 $^{\circ}\text{C}$ using dry ice/ethanol after removal of the remaining water vapor by a Nafion dryer (MD-110-96S; Perma Pure LLC, NJ, USA). The flow rate was regulated (approx. 50 mL min^{-1}) by a needle valve equipped with a flow meter for 20 min. After the flow rate became lower than 10 mL min^{-1} , V4 was opened. The sampling tube was flushed with pure N_2 (>99.99995 vol. %) with 50 mL min^{-1} for 40 min. After the transfer of samples, V6, V7 and V8 were closed. Then OCS was preserved in the adsorption tube. We initially confirmed that OCS did not pass through an adsorption tube at a flow rate lower than 50 mL min^{-1} using two adsorption tubes connected in series from the second adsorption tube: OCS was observed only from the first tube; not from the second tube. For this study, the collected OCS samples in adsorption tubes were measured within 30 min, except for the preservation test.

2.3 Purification system

After sampling OCS from the air using the sampling system as described above, the collected OCS was purified and connected directly to the measurement system. The schematic system is shown in Figure 2. Excluding a fused silica capillary tube, all tubes and valves are made of stainless steel. U-shaped trap 1 is a 50 cm, 1/4 inch (0.64 cm) outer diameter (1/8 inch (0.32 cm) inner diameter) stainless steel tube. U-shaped trap 2 is a 30 cm, 1/8 inch (0.32 cm) outer diameter (1/16 inch (0.16 cm) inner diameter) stainless steel tube filled with Tenax TA (60/80 mesh; GL Science Inc.). Before the experiment, trap 2 is heated to 150 $^{\circ}\text{C}$ by an electric heating mantle (P-22; Tokyo Technological Labo Co., Ltd.) for 30 min at 30 mL min^{-1} with high-purity He for conditioning. Coil-shaped trap 3 is an empty stainless steel tube (1/16 inch (0.16 cm) outer diameter, 50 cm length). Coil-shaped trap 4 is a fused silica capillary tube (0.32 mm inner diameter, 50 cm length, GL Science Inc.). The GC1 (GC-8610T; JEOL Ltd., Tokyo, Japan) is equipped with a column packed with Porapak Q (80/100, GL Science Inc.) (1/8 inch (0.32 cm) outer diameter, 3 m length) to separate OCS from CO_2 . The GC1 oven temperature for OCS purification was programmed to provide 30 $^{\circ}\text{C}$ for 5 min, ramping to 60 $^{\circ}\text{C}$ at 30 $^{\circ}\text{C}$ min^{-1} , followed by ramping to 230 $^{\circ}\text{C}$ at 30 $^{\circ}\text{C}$ min^{-1} from 40 min, and 230 $^{\circ}\text{C}$ for 1 min.

After the adsorption tube containing OCS was connected to the purification system, v3, v4, and v5 were opened and the air in the line was pumped out using a rotary pump (DA-60D; Ulvac Kiko, Miyazaki, Japan) for 5 min; v3, v4, and v5 were then closed. When the adsorption tube was heated at 130 °C and v2, v7, v8, and v6 were opened, gases in the adsorption tube passed through trap 1 cooled by dry ice (-78 °C) to remove trace remnant water vapor. Also, OCS was collected in trap 2, with Tenax TA cooled by dry ice/ethanol (-72 °C) with high-purity He flow rate of 30 mL min⁻¹. After 15 min, port valve (PV) 1 was changed. Trap 2 was then removed from dry ice/ethanol and was heated at 130 °C. The retention times of CO₂ and OCS were initially determined by injecting a mixture of 8 mmol of CO₂ from pure CO₂ in a cylinder (99.995 % purity; Japan Fine Products Co. Ltd.) and 10 nmol of OCS from sample C. They were, respectively, 3–10 min for CO₂ and 20–30 min for OCS at a flow rate of 25 mL min⁻¹. Trap 3 was cooled by liquid N₂ from 10 min; PV2 was changed from 15 min to 35 min after injection of samples to GC1 to introduce OCS to trap 3. OCS with high-purity He was passed through the column and collected in trap 3 for 20 min. After OCS collection in trap 3, the OCS was again transferred to trap 4 in liquid N₂ at 6 mL min⁻¹ by high-purity He with removal of liquid N₂ from trap 3 to a cryofocus. Trap 4 was then removed from liquid N₂; the OCS passed through the GC2 and introduced directly to the detectors (quadrupole mass spectrometer (Q-MS) or IR-MS depending on the experiments explained below).

2.4 Determination of the OCS concentration

The OCS concentrations were measured by GC/Q-MS (7890A; Agilent Technologies Inc., CA, USA coupled to Q-MS, 5975C; Agilent Technologies Inc., CA, USA) equipped with a capillary column (0.32 mm inner diameter, 25 m length, and 10 µm thickness; HP-PLOT Q, Agilent Technologies, CA, USA). The He flow was set to 1.5 mL / min and oven temperature program was set as 60 °C for 15 min, ramped to 230 °C at 60 °C min⁻¹, then 230 °C for 1 min.

To ascertain the OCS concentration of samples A once a month, and to ascertain the collected OCS amounts using a sampling system, we made a calibration curve for OCS ranging 0.1 nmol to 10 nmol using Q-MS. The calibration curve for the nanomole level is made by injection of sample B with a volume of 0.5 mL, 2.2 mL, 4.4 mL, 8.8 mL, 11 mL, 13.2 mL, 17.6 mL, 22 mL, and 44 mL ($n = 3$). The precision (standard deviation (1σ) relative to mean) of the OCS amount by a syringe injection was estimated ± 3 % by the standard deviation of the relative error between the measured values and the estimated value for calibration curves.

To ascertain the OCS concentrations of samples F and G, we prepared calibration curves for OCS ranging 0 pmol to 100 pmol using Q-MS. Calibration curve for the picomole level is made by injection of sample B with volume of 0 µL, 200 µL, 400 µL, and 800 µL ($n = 3$) with precision ± 3 % as estimated similarly above. For determination of OCS concentrations of samples F and G, samples F and G were stored in 50 mL two-neck glass bottles with atmospheric pressure and were introduced to the purification system from an attached glass bottle instead of an adsorption tube. The measured OCS concentrations for samples F and G were, respectively, (380 ± 15) pmol mol⁻¹, and (160 ± 5) pmol mol⁻¹ (Table 2).

The OCS concentrations for the samples F, G, H and I were lower than that of typical atmospheric OCS concentrations (400–550 pmol mol⁻¹) (Montzka et al., 2007), even though the samples were compressed air collected from the ambient atmosphere. Because we were concerned about the changes in OCS concentrations for the samples F and G, the OCS concentrations for the samples F and G were measured at least within a week before or after the experiment. In a similar manner, the cylinders of sample H, I, J, and K were used for experiment within 2–3 days. Therefore, the change of OCS concentration in samples might occur.

2.5 Determination of the sulfur isotope ratios of OCS

For determination of the sulfur isotope ratios of OCS, OCS was passed through the GC2 after a purification system as described above. Then it was introduced directly to the IR-MS (MAT253; Thermo Fisher Scientific Inc., Berlin, Germany) via an open split interface (ConFlo IV; Thermo Fisher Scientific Inc.). Reference OCS of sample A was purified with liquid N₂ (-196 °C) and then introduced via a conventional dual inlet system. Pure OCS is not commercially available in Japan because of its toxicity (Hattori et al. 2015). In addition to the method introducing OCS to IR-MS as described above, conventional syringe injection line, which was previously used for Hattori et al. (2015) and Kamezaki et al. (2016), was also used for comparison or calibration. Briefly, the syringe-injected OCS was collected in stainless steel tubes (10.5 mm inner diameter, 150 mm length) cooled at -196 °C by liquid N₂ with vacuum by a rotary pump (Pascal 2010; Pfeiffer Vacuum GmbH, ABlar, Germany) gently with regulation using a valve. After transfer of OCS to the trap, the two-way six port valve was changed. Then liquid N₂ was removed from the trap. Subsequently, OCS was transferred and collected in a fused silica capillary tube (0.32 mm inner diameter, 50 cm length; GL Science Inc.) covered by a stainless steel tube containing liquid N₂ for 13 min before being introduced into the GC/IR-MS system.

In the IR-MS ion source, electron impact ionization of OCS produced S⁺ fragment ions. The sulfur isotope ratios in OCS were therefore determined by measuring the fragment ions ³²S⁺, ³³S⁺, and ³⁴S⁺ using triple Faraday collector cups. The typical precisions (1σ) of the replicate measurements (n = 3) are, respectively, 0.4 ‰, 0.2 ‰, and 0.3 ‰ for δ³³S(OCS), δ³⁴S(OCS), and Δ³³S(OCS) values. A reference OCS gas was introduced for 20 s at three times started at t = 350 s, 825 s, and 1025 s. The reference gas at t = 350 s was used as the reference for all calculations of OCS sulfur isotope ratios. To remove hydrogen sulfide and ethane from ambient samples, from t = 300 s, the effluent from the GC column was kept off the MS line using back-flushed helium flow. Sulfur isotope ratios are typically reported as

$$\delta^x\text{S} = {}^xR_{\text{sample}} / {}^xR_{\text{standard}} - 1, \quad (1)$$

where ^xR represents the isotopic ratios (^xS/³²S, where x = 33 or 34) of the samples and standards. The sulfur isotope ratios are reported relative to the Vienna Canyon Diablo Troilite (VCDT, quoted as per mil values (‰)). In addition to the δ values, capital delta notation (Δ³³S value) is used to distinguish mass-independent fractionation (MIF; or non-mass-dependent

fractionation) of sulfur, which causes deviation from the mass-dependent fractionation (MDF) line. The $\Delta^{33}\text{S}$ value describes the excess or deficiency of ^{33}S relative to a reference MDF line. It is expressed as

$$\Delta^{33}\text{S} = \delta^{33}\text{S} - [(\delta^{34}\text{S} + 1)^{0.515} - 1]. \quad (2)$$

5 The δ values in this study were determined using the following processes. First, we ascertained the $\delta^{34}\text{S}$ value of sample A by converting OCS to SF_6 . The $\delta^{34}\text{S}(\text{SF}_6)$ value was measured relative to the VCDT scale by comparing SF_6 similarly converted from IAEA-S-1 (Ag_2S : $\delta^{34}\text{S} = -0.30 \text{ ‰}$; Robinson, 1993) as described by Hattori et al. (2015). The measured $\delta^{34}\text{S}$ value of sample A was 12.6 ‰, which was lower than the data presented by Hattori et al. (2015) with 14.3 ‰ (Table 1). Secondly, the $\delta^{34}\text{S}$ value of sample B, which was used as working standard for $\delta^{34}\text{S}$ measurements, were ascertained from
10 comparison with the $\delta^{34}\text{S}$ value (in VCDT scale) of sample A in GC/IR-MS method using S^+ fragment ion. The $\delta^{34}\text{S}(\text{OCS})$ value of sample B in this study was $(14.1 \pm 0.2) \text{ ‰}$ (Table 1), showing no significant difference with the $\delta^{34}\text{S}(\text{OCS})$ value of sample B ($14.3 \pm 0.2) \text{ ‰}$ in data presented by Hattori et al. (2015). It is noteworthy that we also found that the OCS concentration in sample B was not changed. Sample B was used as the daily working standard for GC/IR-MS measurement to ascertain sample $\delta^{34}\text{S}(\text{OCS})$ values for other samples used throughout this study (Table 1).

15 3 Results and Discussion

3.1 Sampling efficiency of OCS

To test the sampling and desorption efficiency, the cylinder containing sample F was connected to a flow meter and the flow was adjusted to 6 L min^{-1} with a needle valve. 5 L min^{-1} were drawn through the sampling system with a pump and the remainder was vented into the air to maintain atmospheric pressure at the sampling inlet. **The samples were collected within**
20 **two days to prevent OCS loss in the cylinder.** The vent flow was measured with a flow meter (ACM-1A; Kofloc, Tokyo, Japan). To ascertain the trapping efficiency OCS was sampled for 10 min, 50 min, and 100 min with blank test intervals as presented in Figure 3a (see section 2.2 for sampling procedure). The sampling times corresponded to sampling volumes of $(50 \pm 2.5) \text{ L}$, $(250 \pm 13) \text{ L}$ and $(500 \pm 25) \text{ L}$ and the respectively and the corresponding OCS amounts were $(0.77 \pm 0.04) \text{ nmol}$, $(3.9 \pm 0.2) \text{ nmol}$, and $(7.7 \pm 0.4) \text{ nmol}$ respectively (Figure 3a).

25 Recovery and precision (1σ) for OCS amounts collected for sampling times of 10 min, 50 min, and 100 min were, $(0.9 \pm 0.1) \text{ nmol}$ ($n = 3$), $(3.6 \pm 0.2) \text{ nmol}$ ($n = 3$) and $(7.4 \pm 0.3) \text{ nmol}$ ($n = 2$), respectively. The OCS blanks were smaller than 15 pmol. These results indicate that yield of OCS during sampling and transferring from the sampling tube to the adsorption tube is almost over 95 %. The memory effect of the system between the sampling run is expected to be less than 1% when sampling OCS amount over 3 nmol (approx. 50 min). Figure 3b presents a comparison of OCS amount between
30 observed OCS amounts and OCS amounts calculated based on OCS concentration in sample F and sampling time, showing that all results fall on the 1:1 line. This suggests that almost 100 % of OCS for sampling runs were collected in the sampling

tube and were transferred successfully to the adsorption tube. Although the collected OCS amount in 10 min was slightly larger than the expected OCS amount, the OCS amounts in 100 min were slightly lower than the expected OCS amount. This result indicates that a small OCS contamination during the sampling and a purification system might exist but that it might not be significant, as discussed above.

5 3.2 Accuracy of the sulfur isotopic analysis of OCS via sampling/purification systems

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. These tests revealed an OCS loss of less than 2 % using a newly developed method and suggest a complete recovery of OCS within the given limits of uncertainty (± 3 %). To assess the dependence of the sulfur isotopic measurements on the OCS amount, different amounts of OCS using sample B were tested. 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 N₂ (> 99.99995 vol. %; Nissan Tanaka Corp., Saitama, Japan) (Figure 1). For each experiment, a total volume of 500 L N₂ was processed. The OCS contamination for this experiment was (0.30 ± 0.16) nmol ($n = 3$) when we flushed with 500 L of pure N₂ stream. For comparison, similar amounts of OCS were also injected using a syringe injection system developed previously (Hattori et al., 2015). Comparisons of OCS concentrations and δ and Δ values are depicted in Figure 4. Although the observed OCS isotope ratios using 3 nmol OCS with the developed method were scattered (1σ uncertainty: 1.0 ‰, 1.0 ‰, and 0.5 ‰, respectively, for $\delta^{33}\text{S}(\text{OCS})$, $\delta^{34}\text{S}(\text{OCS})$, and $\Delta^{33}\text{S}(\text{OCS})$ values), the reproducibilities at the 6 nmol level were sufficient (1σ uncertainty: 0.4 ‰, 0.2 ‰, and 0.4 ‰, respectively, for $\delta^{33}\text{S}(\text{OCS})$, $\delta^{34}\text{S}(\text{OCS})$, and $\Delta^{33}\text{S}(\text{OCS})$ values) and were similar to those obtained with the conventional syringe injection system for Hattori et al. (2015) (Figure 4). Consequently, this system better accommodates OCS samples over 6 nmol, indicating the necessity for collection of ambient air in amounts greater than 300 L.

Furthermore, to test possible sulfur isotopic fractionations during sampling/purification processes, which might change the measurement accuracy, we compared the developed sampling/purification system with the conventional syringe injection system using 8 nmol of the in-house synthesized OCS (samples B, C, D, and E) with triplicates injections. In Figure 5, the $\delta^{34}\text{S}(\text{OCS})$ values measured using the developed sampling/purification system were 0.2 ‰ lower (sample B) but 0.8 ‰, 0.4 ‰, and 0.6 ‰ higher (samples C, D, and E, respectively) than those measured using the syringe injection system of Hattori et al. (2015) (Table 1). This phenomenon was observed similarly for the $\delta^{33}\text{S}(\text{OCS})$ values (Figure 5c), indicating that this process is not isotopic fractionation but that rather suggests contamination during the sampling processes. When

considering (0.30 ± 0.16) nmol OCS (i.e. approx. 4 % for 8 nmol OCS samples) with $\delta^{34}\text{S}$ of 3–18 ‰ covering reported $\delta^{34}\text{S}$ range of OCS sources (Newman et al., 1990), the accuracy of the $\delta^{34}\text{S}(\text{OCS})$ can be shifted -0.3 to $+0.3$ ‰. Because the precision of 1σ uncertainty is 0.2 ‰, the overall precision values (1σ) for $\delta^{34}\text{S}$ of this sampling/purification system were estimated as 0.4 ‰.

5 3.3 Sulfur isotope ratio for atmospheric OCS

Four ambient air samples were collected at the Suzukakedai campus of Tokyo Institute of Technology located in Yokohama, Japan (35.5°N , 139.5°W , 27 m height) during 23–25 April 2018 every 12 h (sampling times were 23 April 2018 12:00, 24 April 2018 00:00, 24 April 2018 12:00, and 25 April 2018 00:00). The sampling volume was 500 L (i.e. 100 min with a pump flow of 5 L min^{-1}). Measurements of OCS concentrations and sulfur isotope ratios were carried out within 30 min after the sampling. The time for single measurement of $\delta^{34}\text{S}$ value for atmospheric OCS was 100 min (500 L) for sampling of air, 40 min for transferring to the absorption tube, 40 min for purification, and 20 min for measurement using IR-MS. The OCS concentrations and $\delta^{34}\text{S}(\text{OCS})$ values observed for ambient air are presented in Figure 6.

In contrast to the $\delta^{34}\text{S}(\text{OCS})$ value, the $\delta^{33}\text{S}(\text{OCS})$ value in air was not determined because of the unexpected peak (approx. 40 mV height) observed for m/z 33, which slightly overlapped the OCS peak of the chromatogram (Figure 7). We notably didn't observe any interferences on m/z 32 and m/z 34. The interfering compound could have not yet been identified. Known fragments interfering on m/z 33 are CH_3O^+ originating from the protonation of methanol and/or the reaction of CH_3^+ with H_2O , CH_2F^+ that is indicative hydrofluorocarbons, and/or NF^+ deriving from nitrogen trifluoride (NF_3). To measure m/z 33 of OCS without interferences, further improvement of peak separation of OCS with interferences is required by changing parameter of the separation in the system and/or data processing. For example, custom made MATLAB routine, which can extrapolate the peak tail of interference via an exponentially decaying function to distinguish the two gaseous species as described in Zuiderweg et al. (2013), would enable us to analyze m/z 33 in addition to the standard ISODAT software used for isotope ratio measurements.

The observed OCS concentrations for atmospheric samples were 447–520 pmol mol^{-1} (Figure 6a), averaging $(492 \pm 34) \text{ pmol mol}^{-1}$. Data show no clear differences between 0:00 and 12:00 in two days (p -value = 0.65). This OCS concentration observed at Suzukakedai campus shows good agreement with the OCS concentrations observed at similar latitude in USA (e.g. 400–550 pmol mol^{-1} ; Montzka et al., 2007). Berkelhammer et al. (2014) reported diurnal variation for OCS concentrations in USA with the lowest at 8:00 and the highest at 16:00 with 80 pmol mol^{-1} changes in a day. Moreover, the differences of OCS concentrations for four atmospheric samples were less than 80 pmol mol^{-1} . The observed $\delta^{34}\text{S}(\text{OCS})$ values of four atmospheric samples were 10.4–10.7 ‰ (Figure 6b) and averaged $(10.5 \pm 0.4) \text{ ‰}$. The $\delta^{34}\text{S}(\text{OCS})$ values also showed no clear diurnal difference (p -values = 0.29) (Figure 6b). Given the diurnal OCS variations, some future study is clearly necessary to ascertain whether or not $\delta^{34}\text{S}(\text{OCS})$ values have diurnal variations by comparing $\delta^{34}\text{S}(\text{OCS})$ values for the highest OCS concentration at 8:00 and the lowest OCS concentration at 16:00.

It is noteworthy that the $\delta^{34}\text{S}(\text{OCS})$ values of four atmospheric samples were clearly distinct from our earlier observed $\delta^{34}\text{S}(\text{OCS})$ value of $(4.9 \pm 0.3) \text{‰}$ obtained from sample G (Hattori et al., 2015), that was postulated as a global representative $\delta^{34}\text{S}(\text{OCS})$ value in the atmosphere. In fact, the OCS concentrations in the commercial cylinders F, G and H were significantly lower than typical atmospheric OCS concentrations of approx. $500 \text{ nmol mol}^{-1}$ (Table 2). Ascertaining the $\delta^{34}\text{S}(\text{OCS})$ value in sample G using the current sampling/purification system yielded a $\delta^{34}\text{S}(\text{OCS})$ value of $(6.1 \pm 0.2) \text{‰}$ being slightly higher than the previous value of $(4.9 \pm 0.3) \text{‰}$ (Hattori et al., 2015). It is possible to explain this 1.2 ‰ increase for $\delta^{34}\text{S}(\text{OCS})$ value for a case in which the contaminated OCS has $\delta^{34}\text{S}(\text{OCS})$ value with over 17 ‰. However, such a high $\delta^{34}\text{S}(\text{OCS})$ value from contamination requires a situation in which the contaminated OCS come only from the ocean, which is not likely. Because the atmospheric $\delta^{34}\text{S}(\text{OCS})$ values in this study were $(10.5 \pm 0.4) \text{‰}$ and higher than that for sample G, the increased $\delta^{34}\text{S}(\text{OCS})$ values are expected to be affected by isotopic fractionation during OCS degradation in the cylinder and not by contamination. The causes for the OCS losses in the commercial pressurized air cylinders could not be investigated here. Indeed, as reported by Kamezaki et al. (2016), OCS is decomposed by hydrolysis, which increases the $\delta^{34}\text{S}(\text{OCS})$ value. Additionally, observation of OCS loss caused by adsorption to walls in the canister was reported by Khan et al. (2012). The compressed air of samples F and G might be affected by anthropogenic OCS sources at the sampling site and/or during the compressing processes. All in all, the $\delta^{34}\text{S}(\text{OCS})$ value of sample G is no longer considered as a representative of atmospheric OCS.

3.4 Preservation tests

As described above, we measured OCS concentration and sulfur isotope ratio of atmospheric samples within 30 min after sampling. The OCS concentrations are consistent with the observed OCS concentrations in the same latitude and our tests revealed no OCS losses under these conditions. However, after the development of the system, we realized up to 50 % of OCS can be decomposed during storage of the adsorption tube after we have measured the samples within 14 days after sampling (Figure 8a). We also found that the OCS in the stainless steel adsorption tubes stored at 25 °C showed only slight changes in concentration with $(-6 \pm 6) \%$ and for $\delta^{34}\text{S}(\text{OCS})$ values with $(0.2 \pm 0.4) \text{‰}$ after 3 h (Figure 8b). All data sets presented up to this point were undertaken immediately after the sampling (i.e. shorter than 30 min.). Therefore, we did not expect marked changes in OCS concentrations and the $\delta^{34}\text{S}(\text{OCS})$ values for most datasets including atmospheric OCS samples. Because OCS is known to react with the surface of stainless steel (Khan et al., 2012), for future use, this fact requires appropriate ways of preservation of OCS during transportation from field sampling sites to laboratory until analysis.

In order to minimize potential OCS decomposition on the surface wall, we modified the adsorption tube by replacing the stainless steel tube and valves by a Sulfinert-treated tube and Sulfinert-treated valves. The preservation of OCS on the modified sampling tubes at different storage temperatures using samples H, I, J and K. The samples were processed as that described in section 2.2 and transferred to the adsorption tubes. The adsorption tubes were stored at temperatures of

25 °C, 4 °C, -20 °C and -80 °C, respectively, until measurements. After each storage period, the samples were analyzed for OCS yields and $\delta^{34}\text{S}(\text{OCS})$ values as described in sections 2.3, 2.4, and 2.5. A rapid OCS decomposition of approximately 20 % during 7 days of storage was observed for the stainless steel adsorption tubes stored at 25 °C. A similar pronounced loss was observed for the Sulfinert-treated adsorption tubes stored at 4 °C but at a storage temperature of -20 °C. The OCS was stable for 30 days at -20 °C, and for at least 90 days at -80 °C within 1σ uncertainty of 6 % (Figure 8a). Furthermore, we found that the $\delta^{34}\text{S}(\text{OCS})$ values showed no significant change during storage for at least 14 days at -80 °C (Figure 8b). These results demonstrate that it is possible to apply this method for field campaigns by storing the adsorption tube at -80 °C after sampling.

3.5 Atmospheric implications

10 The $\delta^{34}\text{S}(\text{OCS})$ value of $(10.5 \pm 0.4) \text{‰}$ is generally consistent with earlier estimation by Newman et al. (1991), who expected the mean $\delta^{34}\text{S}(\text{OCS})$ values of 11 ‰ based on the flux of continental emission as 3 ‰ and oceanic emission as 18 ‰ (Newman et al., 1991). This estimation is based on older information, but current measurements of atmospheric DMS and DMSP are similar to 18 ‰ (Said-Ahmad and Amrani, 2013; Amrani et al., 2013; Oduro et al., 2012); continental sulfur sources also show approx. 0–5 ‰ (Tcherkez and Tea, 2013).

15 It is noteworthy that the potential importance of tropospheric sulfur isotopic fractionations during OCS sinks. To date, sulfur isotopic fractionations were reported as -5 to 0 ‰ for reaction with OH radical (Schmidt et al., 2012), and for -2 to -4 ‰ for decomposition by soil microorganisms (Kamezaki et al., 2016; Ogawa et al., 2017), respectively. Sulfur isotopic fractionation for OCS by plant uptake, dominant OCS sink in troposphere (Berry et al., 2013), have not been determined, but the theoretical isotopic fractionation constant by plant uptake is -5.3 ‰ (Angert et al., 2018). Therefore, all sulfur isotopic
20 fractionation constants by OCS degradation are negative, indicating that the $\delta^{34}\text{S}(\text{OCS})$ values can be increased by OCS degradation in the troposphere. Because the main OCS sink is photosynthesis by plants, the $\delta^{34}\text{S}(\text{OCS})$ values in the atmosphere might be increased in the growing season for plants in April. However, because of the long lifetime of OCS, $\delta^{34}\text{S}(\text{OCS})$ values might not be sensitive to seasonal variation. Future studies must be conducted to determine the isotopic fractionation constants and observations of $\delta^{34}\text{S}(\text{OCS})$ values to estimate the dynamics of atmospheric $\delta^{34}\text{S}(\text{OCS})$ values in
25 the troposphere.

In addition to our observation of atmospheric $\delta^{34}\text{S}(\text{OCS})$ values with $(10.5 \pm 0.4) \text{‰}$ at Suzukakedai campus, Yokohama, Japan, recently $\delta^{34}\text{S}(\text{OCS})$ values with $(13.4 \pm 0.5) \text{‰}$ in August–October at Israel, $(12.8 \pm 0.5) \text{‰}$ in February–March in Israel, and $(13.1 \pm 0.7) \text{‰}$ in February–March at the Canary Islands, Spain were reported using GC/MC-ICP-MS method (Angert et al., 2018). These differences indicate that the atmospheric $\delta^{34}\text{S}(\text{OCS})$ values might not be homogeneous,
30 instead reflecting some geographic effects and/or potential difference for isotopic fractionations during sink processes. Given the higher influences of sulfur isotopic fractionations on $\delta^{34}\text{S}(\text{OCS})$ values during growing seasons, it is not likely to explain

lower atmospheric $\delta^{34}\text{S}(\text{OCS})$ values for Suzukakedai campus in April from those for Israel and Canary Islands observed in February–March. Rather, $\delta^{34}\text{S}(\text{OCS})$ values with $(10.5 \pm 0.4) \text{‰}$ at Suzukakedai campus might be more affected by anthropogenic OCS emission and/or less affected by oceanic OCS emissions compared to the samples collected in Israel/ Canary Islands with higher $\delta^{34}\text{S}(\text{OCS})$ values. Potential anthropogenic OCS sources are Chinese emissions from rayon (yarn and staple) and coal (industry and residential), as pointed out by recent OCS source inventories (Zumkher et al., 2018). In fact, the OCS concentration in the vicinity of China is high based on satellite observation (Glatthor et al., 2015). Future study is necessary to observe spatial and temporal variation of $\delta^{34}\text{S}(\text{OCS})$ values to discuss the link between anthropogenic activity and OCS cycles.

In addition to tropospheric OCS sources, OCS have some potential as tracers of net ecosystem exchange into gross primary production (GPP) on land (Campbell et al., 2008). Based on our earlier experiments, to elucidate OCS in the troposphere and its relation to biochemical activity by plant and soil microorganisms, OCS sulfur isotope analysis provides a new tool to investigate soil OCS sinks in the troposphere. To date, we have determined the isotopic fractionation constants for OCS undergoing bacterial OCS degradation and its enzyme (Kamezaki et al., 2016; Ogawa et al., 2017). Similarly, additional studies that include specific examination of isotopic fractionation by plant uptake, another major sink of atmospheric OCS, are indispensable for distinguishing the respective OCS fluxes of soil and plants. By coupling isotopic fractionations by soil and plant with atmospheric observations of $\delta^{34}\text{S}(\text{OCS})$ values using our newly developed method, the atmospheric observations of $\delta^{34}\text{S}(\text{OCS})$ values are expected to help refine estimates of biological activities of plant and soil microorganisms and their respective contributions to OCS degradation in the troposphere.

3.6 Comparison with other methods

We here discuss the comparison of this sampling system coupled with GC/IR-MS and GC/MC-ICP-MS method (Said-Ahmad et al., 2017; Angert et al., 2018). The required sample amounts for our IR-MS system of over 6 nmol OCS. The overall precision value (1σ) for atmospheric $\delta^{34}\text{S}(\text{OCS})$ value is 0.4 ‰. By contrast, GC/MC-ICP-MS method (Said-Ahmad et al., 2017; Angert et al., 2018) has similar precision of 0.6 ‰, but only requires 20 pmol OCS. Consequently, IR-MS method requires a 300 times larger sample OCS than GC/MC-ICP-MS method. Therefore, our IR-MS method with a developed large volume air sampling system, has shortcomings for sample size and/or logistics for field campaigns. However, it is worth noting that benefits of our IR-MS method with its large volume air sampling system include its potential application of multi-isotope measurements of OCS by measuring CO^+ fragment ions for carbon and oxygen isotopes as well as S^+ fragment ions.

4 Summary

For this study, we developed a new OCS sampling and purification system. OCS is extracted from 500 L of ambient air with a collection efficiency of almost over 95 % of OCS. The blank of the sampling and purification system was (0.30 ± 0.16) nmol and memory effects were negligible. By comparison with the previous used syringe injection (Hattori et al., 2015) we demonstrated that any potential isotopic fractionation during sampling and purification is negligible. The analytical repeatability values (1σ) for $\delta^{34}\text{S}(\text{OCS})$ value with more than 6 nmol for the commercial OCS samples and synthesized OCS samples were 0.2 ‰. We ascertained the $\delta^{34}\text{S}(\text{OCS})$ values for four atmospheric samples at Suzukakedai campus of Tokyo Institute of Technology located in Yokohama, Kanagawa, Japan. $\delta^{33}\text{S}(\text{OCS})$ were not reported because of a small overlapping signal on m/z : 33 in the ambient air samples. The OCS concentrations and $\delta^{34}\text{S}(\text{OCS})$ values respectively, were in the range of 447–520 pmol mol⁻¹ and 10.4–10.7 ‰. No clear diurnal variation in the $\delta^{34}\text{S}(\text{OCS})$ values was observed. Further modification of gas chromatographic techniques and/or data processing must be undertaken to measure $\delta^{33}\text{S}(\text{OCS})$ and $\Delta^{33}\text{S}(\text{OCS})$ values in future studies.

We earlier proposed a $\delta^{34}\text{S}(\text{OCS})$ value of (4.9 ± 0.3) ‰ for atmospheric OCS from measurements from a commercially available cylinder of compressed air (sample G in this study) (Hattori et al. 2015). Based on the four atmospheric samples taken in this study we revise this earlier value to (10.5 ± 0.4) ‰ being clearly distinct from the earlier value. The new $\delta^{34}\text{S}(\text{OCS})$ proposed here is in accordance with the $\delta^{34}\text{S}(\text{OCS})$ estimates of tropospheric and marine sources of OCS based on the OCS flux (Newman et al., 1991). Although OCS decomposition during preservation before the measurements was concerned, we found that no such OCS decomposition and isotopic fractionation have been observed for the modified adsorption tube made by Sulfinert-treated tube and valves and preservation at -80 °C at least within 90 days for OCS concentration and up to 14 days for $\delta^{34}\text{S}(\text{OCS})$ values.

Recently, Angert et al. (2018) reported the $\delta^{34}\text{S}(\text{OCS})$ value of ~ 13 ‰ in Israel or Canary Islands, and they suggested that the $\delta^{34}\text{S}(\text{OCS})$ value is homogeneous throughout the world. Although it is difficult to identify the reason for the difference of atmospheric $\delta^{34}\text{S}(\text{OCS})$ values between 10.5 ‰ in Japan and ~ 13 ‰ in Israel or Canary Islands, spatial and temporal variation of $\delta^{34}\text{S}(\text{OCS})$ values are expected to be a link between anthropogenic activities and OCS cycles.

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References

- 5 Amrani, A., Said-Ahmad, W., Shaked, Y., and Kiene, R. P.: Sulfur isotope homogeneity of oceanic DMSP and DMS, Proc. Natl. Acad. Sci. U.S.A., 110(46), 18,413–18,418, 2013.
- Angert, A., Said-Ahmad, W., Davidson, C., and Amrani A.: Sulfur isotopes ratio of atmospheric carbonyl sulfide constrains its sources, *Scientific Reports*, 9(741), 1-8, 2018.
- Bahlmann, E., Weinberg, I., Seifert, R., Tubbesing, C., and Michaelis W.: A high volume sampling system for isotope determination of volatile halocarbons and hydrocarbons, *Atmos. Meas. Tech.*, 4, 2073–2086, 2011.
- 10 Berkelhammer, M., Asaf, D. Still, C., Montzka, S., Noone, D., Gupta, M., Provencal, R., Chen, H. and Yakir, D.: Constraining surface carbon fluxes using in situ measurements of carbonyl sulfide and carbon dioxide, *Global Biogeochem. Cycles*, 28, 161–179, 2014. doi:10.1002/2013GB004644.
- Berry, J., Wolf, A., Campbell, J. E., Baker, I., Blake, N., Blake, D., Denning, A. S., Kawa, S. R., Montzka, S. A., Seibt, U., 15 Stimler, K., Yakir, D., and Zhu, Z.: A coupled model of the global cycles of carbonyl sulfide and CO₂: A possible new window on the carbon cycle, *J. Geophys. Res. - Biogeo.*, 118, 842–852, 2013.
- Brenninkmeijer, C. A. M., Janssen, C., Kaiser, J., Rockmann, T., Rhee, T. S., and Assonov, S. S.: Isotope effects in the chemistry of atmospheric trace compounds, *Chem. Rev.*, 103 (12), 5125–5161, 2003.
- Brühl, C., Lelieveld, J., Crutzen, P. J., and Tost, H.: The role of carbonyl sulphide as a source of stratospheric sulphate 20 aerosol and its impact on climate, *Atmos. Chem. Phys.*, 12 (3), 1239–1253, 2012.
- Campbell, J. E., Carmichael, G. R., Chai, T., Mena-Carrasco, M., Tang, Y., Blake, D. R., Blake, N. J., Vay, S. A., Collatz, G. J., Baker, I., Berry, J. A., Montzka, S. A., Sweeney, C., Schnoor, J. L., and Stanier, C. O.: Photosynthetic Control of Atmospheric Carbonyl Sulfide During the Growing Season, *Science*, 322, 1085–1088, 2008.
- Castleman, J. A. W., Munkelwitz, H. R., and Manowitz, B.: Isotopic studies of the sulfur component of the stratospheric 25 aerosol layer, *Tellus*, 26, 222–234, 1974.
- Chin, M. and Davis, D. D.: A reanalysis of carbonyl sulfide as a source of stratospheric background sulfur aerosol, *J. Geophys. Res.*, 100 (D5), 8993–9005, 1995.
- Commane, R., Meredith, L. K., Baker, I. T., Berry, J. A., Munger, J. W., Montzka, S. A., Templer, P. H., Juice, S. M., Zahniser, M. S., and Wofsy, S. C.: Seasonal fluxes of carbonyl sulfide in a midlatitude forest, *Proc. Natl. Acad. Sci. USA*, 112, 14162–14167, doi:10.1073/pnas.1504131112, 2015.
- 30 Crutzen, P. J.: Possible importance of CSO for sulfate layer of stratosphere, *Geophys. Res. Lett.*, 3 (2), 73–76, 1976.
- Ferm, R. J.: The Chemistry of Carbonyl Sulfide, *Chem. Rev.*, 57 (4), 621–640, 1957.

- Glatthor, N., Höpfner, M., Baker, I. T., Berry, J., Campbell, J. E., Kawa, S. R., Krysztofiak, G., Leyser, A., Sinnhuber, B.-M., Stiller, G. P., Stonecipher, J., and von Clarmann, T.: Tropical sources and sinks of carbonyl sulfide observed from space, *Geophys. Res. Lett.*, 42, 10082–10090, <https://doi.org/10.1002/2015GL066293>, 2015.
- 5 Hattori, S., Danielache, S. O., Johnson, M. S., Schmidt, J. A., Kjaergaard, H. G., Toyoda, S., Ueno, Y., and Yoshida, N.: Ultraviolet absorption cross sections of carbonyl sulfide isotopologues OC³²S, OC³³S, OC³⁴S and O¹³CS: isotopic fractionation in photolysis and atmospheric implications, *Atmos. Chem. Phys.*, 11 (19), 10293–10303, 2011.
- Hattori, S., Schmidt, J. A., Mahler, D. W., Danielache, S. O., Johnson, M. S., and Yoshida, N.: Isotope Effect in the Carbonyl Sulfide Reaction with O(³P), *J. Phys. Chem. A*, 116 (14), 3521–3526, 2012.
- 10 Hattori, S., Toyoda, A., Toyoda, S., Ishino, S., Ueno, Y., and Yoshida, N.: Determination of the Sulfur Isotope Ratio in Carbonyl Sulfide Using Gas Chromatography/Isotope Ratio Mass Spectrometry on Fragment Ions ³²S⁺, ³³S⁺, and ³⁴S⁺, *Anal. Chem.*, 87 (1), 477–484, 2015.
- Inomata, Y., Matsunaga, K., Murai, Y., Osada, K., and Iwasaka, Y. J.: Simultaneous measurement of volatile sulfur compounds using ascorbic acid for oxidant removal and gas chromatography – flame photometric detection, *Chromatogr A*, 864, 111–119, 1999.
- 15 Johnson, M. S., Feilberg, K. L., von Hessberg, P., and Nielsen, O. J.: Isotopic processes in atmospheric chemistry, *Chem. Soc. Rev.*, 31, 313–323, 2002.
- Kamezaki, K., Hattori, S., Ogawa, T., Toyoda, S., Kato, H., Katayama, Y., and Yoshida, N.: Sulfur isotopic fractionation of carbonyl sulfide during degradation by soil bacteria, *Environ. Sci. Technol.*, 50, 3537–3544, 2016.
- Kato, H., Igarashi, Y., Dokiya, Y., and Katayama, Y.: Vertical distribution of carbonyl sulfide at Mt. Fuji, Japan, *Water, Air, Soil Pollut.*, 223 (1), 159–167, 2012.
- 20 Khan, M. A. H., Whelan, M.E., and Rhew R. C.: Analysis of low concentration reduced sulfur compounds (RSCs) in air: Storage issues and measurement by gas chromatography with sulfur chemiluminescence detection, *Talanta*, 88, 581–586, 2012.
- Kremser, S., Jones, N. B., Palm, M., Lejeune, B., Wang, Y., Smale, D., and Deutscher, N. M.: Positive trends in Southern Hemisphere carbonyl sulfide, *Geophys. Res. Lett.*, 42, 9473–9480, <https://doi.org/10.1002/2015GL065879>, 2015.
- 25 Kuai, L., Worden, J., Kulawik, S. S., Montzka, S. A., and Liu, J.: Characterization of Aura TES carbonyl sulfide retrievals over ocean, *Atmos. Meas. Tech.*, 7, 163–172, [doi:10.5194/amt-7-163-2014](https://doi.org/10.5194/amt-7-163-2014), 2014.
- Leung, F.-Y. T., Colussi, A. J., Hoffmann, M. R., and Toon, G. C.: Isotopic fractionation of carbonyl sulfide in the atmosphere: Implications for the source of background stratospheric sulfate aerosol, *Geophys. Res. Lett.*, 29, 1474, 2002.
- 30 Lin, Y., Sim, M. S., and Ono, S.: Multiple-sulfur isotope effects during photolysis of carbonyl sulfide, *Atmos. Chem. Phys.*, 11 (19), 10283–10292, 2011.

- Montzka, S. A., Aydin, M., Battle, M., Butler, J. H., Saltzman, E. S., Hall, B. D., Clarke, A. D., Mondeel, D., and Elkins J. W.: A 350-year atmospheric history for carbonyl sulfide inferred from Antarctic firn air and air trapped in ice, *J. Geophys. Res.*, 109, D22302, doi:10.1029/2004JD004686, 2004.
- Montzka, S. A., Calvert, P., Hall, B. D., Elkins, J. W., Conway, T. J., Tans, P. P., and Sweeney, C.: On the global distribution, seasonality, and budget of atmospheric carbonyl sulfide (COS) and some similarities to CO₂, *J. Geophys. Res.-Atmos.*, 112, D09302, doi:10.1029/2006JD007665, 2007.
- Newman, L., Krouse, H. R., and Grinenko, V. A.: *Stable Isotopes: NAACO; Scope*; John Wiley and Sons, Chapter 5 Sulphur Isotope Variations Atmosphere, 133–176, 1991.
- Oduro, H., Van Alstyne, K. L., and Farquhar, J.: Sulfur isotope variability of oceanic DMSP generation and its contributions to marine biogenic sulfur emissions, *Proc. Natl. Acad. Sci. U.S.A.*, 109(23), 9012–9016, 2012.
- Ogawa, T., Hattori, S., Kamezaki, K., Kato, H., Yoshida, N., and Katayama, Y.: Isotopic fractionation of sulfur in carbonyl sulfide by carbonyl sulfide hydrolase of *Thiobacillus thiooparus* THI115, *Microbes Environ.*, 32, 367–375, 2017.
- Ono, S., Shanks III, W. C., Rouxel, O. J., Rumble, D.: S-33 constraints on the seawater sulfate contribution in modern seafloor hydrothermal vent sulfides, *Geochimica et Cosmochimica Acta*, 71, 1170–1182, 2007.
- Robinson, B. W., *Sulfur isotope standards, Reference and intercomparison materials for stable isotopes of light elements, in Proceedings of a Consultants Meeting Held in Vienna, 1–3 December, 39–46, 1993.*
- Said-Ahmad, W., and Amrani, A.: A sensitive method for the sulfur isotope analysis of dimethyl sulfide and dimethylsulfoniopropionate in seawater, *Rapid Commun. Mass Spectrom.*, 27(24), 2789–2796, 2013.
- Said-Ahmad, W., Wong, K., Mcnall, M., Shawar, L., Jacksier, T., Turich, C., Stankiewicz, A., and Amrani, A.: Compound-Specific Sulfur Isotope Analysis of Petroleum Gases, *Anal. Chem.*, 89, 3199–3207, 2017.
- Sandoval-Soto, L., Stanimirov, M., von Hobe, M., Schmitt, V., Valdes, J., Wild, A., and Kesselmeier, J.: Global uptake of carbonyl sulfide (COS) by terrestrial vegetation: Estimates corrected by deposition velocities normalized to the uptake of carbon dioxide (CO₂), *Biogeosciences*, 2, 125–132, doi:10.5194/bg-2-125-2005, 2005.
- Schmidt, J. A., Johnson, M. S., Hattori, S., Yoshida, N., Nanbu, S., and Schinke, R.: OCS photolytic isotope effects from first principles: sulfur and carbon isotopes, temperature dependence and implications for the stratosphere, *Atmos. Chem. Phys.*, 13 (3), 1511–1520, 2013.
- Schmidt, J. A., Johnson, M. S., Jung, Y., Danielache, S. O., Hattori, S., and Yoshida, N.: Predictions of the sulfur and carbon kinetic isotope effects in the OH + OCS reaction, *Chem. Phys. Lett.*, 531, 64–69, 2012.
- Suntharalingam, P., Kettle, A. J., Montzka, S. M., and Jacob, D. J.: Global 3-D model analysis of the seasonal cycle of atmospheric carbonyl sulfide: Implications for terrestrial vegetation uptake, *Geophys. Res. Lett.*, 35, L19801, <https://doi.org/10.1029/2008GL034332>, 2008.
- Tcherkez, G. and Tea, I.: ³²S/³⁴S isotope fractionation in plant sulphur metabolism, *New Phytologist*, 200: 44–53, 2013.
- Xu, X., Bingemer, H. G., and Schmidt, U.: The flux of carbonyl sulfide and carbon disulfide between the atmosphere and a spruce forest, *Atmos. Chem. Phys.*, 2, 171–181, <https://doi.org/10.5194/acp-2-171-2002>, 2002.

Watts, S. F.: The mass budgets of carbonyl sulfide, dimethyl sulfide, carbon disulfide and hydrogen sulfide, *Atmos. Environ.*, 34 (5), 761–779, 2000

Zuiderweg, A., Holzinger, R., Martinerie, P., Schneider, R., Kaiser, J., Witrant, E., Etheridge, D., Petrenko, V., Blunier, T., and Röckmann, T.: Extreme ^{13}C depletion of CCl_2F_2 in firn air samples from NEEM, Greenland, *Atmos. Chem. Phys.*, 13(2), 599–609, doi:10.5194/acp-13-599-2013, 2013.

5

Zumkehr, A., Hilton, T. W., Whelan, M., Smith, S., Kuai, L., Worden, J., and Campbell, J. E.: Global gridded anthropogenic emissions inventory of carbonyl sulfide, *Atmos. Environ.*, 183, 11-19, 2018.

Table 1: OCS samples balanced with He and synthesized OCS sample of averages and standard deviations (1σ) for sulfur isotope ratios for OCS measured for this study (sampling/purification system with GC/IR-MS) and by conventional syringe injection system with GC/IR-MS as described by Hattori et al. (2015)

Sample	Sample type	Concentration	Supplier	This study												Mode
				DI-IR-MS (SF ₆) ^a			Syringe injection system with GC/IR-MS (S ⁺) ^b			Sampling/Purification system with GC/IR-MS (S ⁺)			S			
				<i>n</i>	$\delta^{33}\text{S}$	$\delta^{34}\text{S}$	$\Delta^{33}\text{S}$	<i>n</i>	$\delta^{33}\text{S}$	$\delta^{34}\text{S}$	$\Delta^{33}\text{S}$	<i>n</i>		$\delta^{33}\text{S}$	$\delta^{34}\text{S}$	
					(‰)	(‰)	(‰)		(‰)	(‰)	(‰)		(‰)	(‰)	(‰)	
A	Commercial cylinder (Balanced with He)	10.50%	-	1	6.5 ^a	12.6 ^a	0.03 ^a	3	6.5 ± 0.2	12.6 ± 0.4	0.03 ± 0.1	-	-	-	-	6
B	Commercial cylinder (Balanced with He)	5.9 μmol mol ⁻¹	-	-	-	-	-	3	7.0 ± 0.1 ^c	14.1 ± 0.2 ^c	-0.2 ± 0.1 ^c	3	6.9 ± 0.4 ^d	13.8 ± 0.4 ^d	-0.2 ± 0.4 ^d	3
C	Synthesized (CO + S reaction)	100%	Wako	-	-	-	-	3	-3.3 ± 0.1 ^d	-6.3 ± 0.2 ^d	-0.06 ± 0.1 ^d	3	-2.8 ± 0.2 ^d	-5.5 ± 0.4 ^d	0.03 ± 0.2 ^d	-
D	Synthesized (CO + S reaction)	100%	Sigma-Aldrich	-	-	-	-	3	1.1 ± 0.2 ^d	2.4 ± 0.2 ^d	-0.07 ± 0.1 ^d	3	1.5 ± 0.4 ^d	2.8 ± 0.7 ^d	0.08 ± 0.1 ^d	-
E	Synthesized (CO + S reaction)	100%	Mixture of Wako and Sigma-Aldrich	-	-	-	-	3	-1.5 ± 0.1 ^d	-2.5 ± 0.2 ^d	-0.2 ± 0.1 ^d	3	-0.8 ± 0.6 ^d	-1.9 ± 0.6 ^d	-0.2 ± 0.3 ^d	-

^a $\delta^{33}\text{S}(\text{SF}_6)$, $\delta^{34}\text{S}(\text{SF}_6)$, and $\Delta^{33}\text{S}(\text{SF}_6)$ values chemically converted from OCS in Sample A was corrected to values relative to the international standard (VCDT) notation by using sample A measured in this study. $\delta^{33}\text{S}(\text{SF}_6)$ converted from IAEA-S-1(Ag₂S: $\delta^{33}\text{S} = -0.055$ ‰ (Ono et al., 2007), $\delta^{34}\text{S} = -0.30$ ‰ (Robinson, 1993) and $\Delta^{33}\text{S} = -0.100$ ‰ (Ono et al., 2007)) and standard deviation (1σ) of 25 times repeated measurement was 0.01 ‰.

^b Developed system by Hattori et al. (2015)

^c Corrected to values relative to the international standard (VCDT) notation by using sample A measured in this study

^d Corrected to values relative to the international standard (VCDT) notation by using daily sample B injected from line developed by Hattori et al. (2015)

^e Averaged and precision of $\delta^{34}\text{S}(\text{SF}_6)$ value chemically converted from OCS in Sample A was corrected to values relative to the international standard (VCDT) notation by using sample A measured in this study. $\delta^{34}\text{S}(\text{SF}_6)$ converted from IAEA-S-1(Ag₂S: $\delta^{33}\text{S} = -0.055$ ‰ (Ono et al., 2007), $\delta^{34}\text{S} = -0.30$ ‰ (Robinson, 1993) and $\Delta^{33}\text{S} = -0.100$ ‰ (Ono et al., 2007)) and standard deviation (1σ) of 25 times repeated measurement was 0.01 ‰.

Table 2: Sample information for compressed air in cylinders collected at Kawasaki, Japan

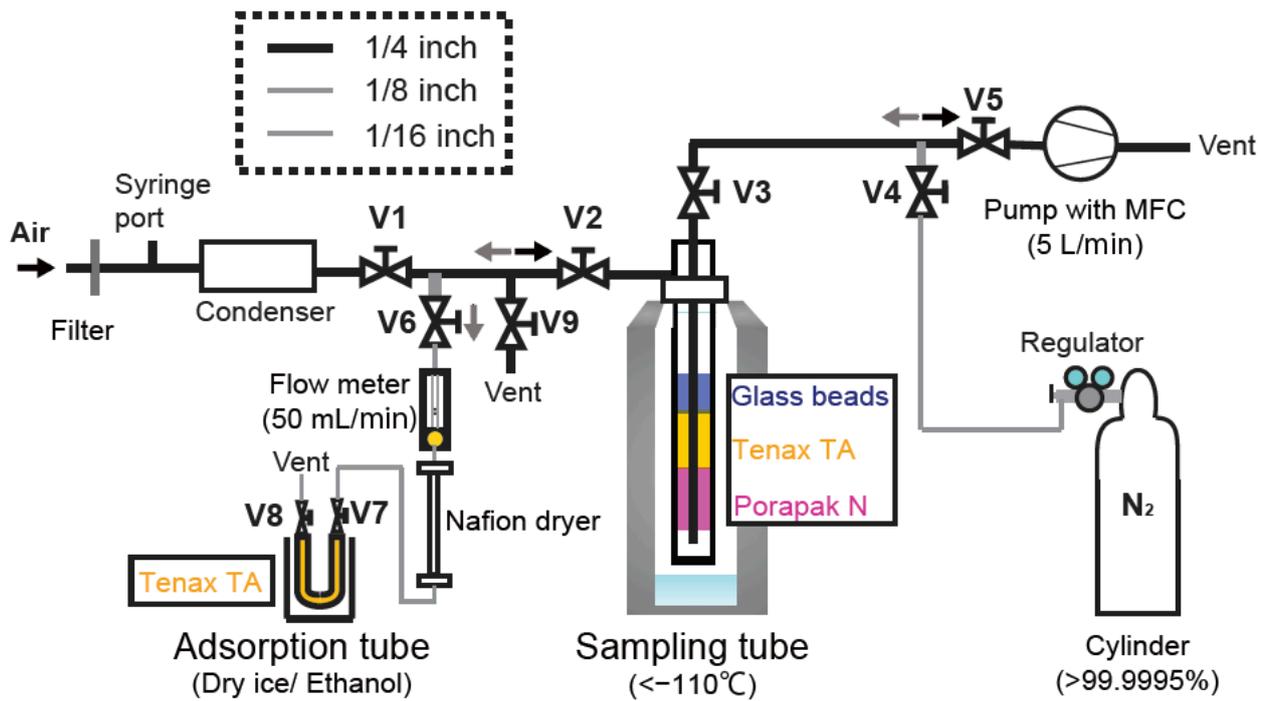
Sample	Concentration pmol mol ⁻¹	$\delta^{34}\text{S}(\text{OCS})$ ‰	Experiments	Collecting date
F	380 ± 15 ^a	11.7 ± 0.4	Test of collection efficiency	25 July 2017
G	168 ± 5 ^a	6.1 ± 0.4 ^d	Determination of sulfur isotopic composition	02 July 2012
H	200 ± 7 ^b	-	Preservation test for OCS amount	02 December 2017
I	371 ± 25 ^{b,c}	9.5 ± 0.4	Preservation test for OCS amount	26 October 2018
J	496 ± 30 ^c	9.3 ± 0.4	Preservation test for OCS amount and $\delta^{34}\text{S}(\text{OCS})$ value	01 December 2018
K	460 ± 29 ^c	10.4 ± 0.4	Preservation test for OCS amount and $\delta^{34}\text{S}(\text{OCS})$ value	26 December 2018

^a Measured using Q-MS with pmol-level calibration curve

^b Measured using Q-MS with nmol-level calibration curve after sampling

^c Measured using IR-MS with calibration curve in Figure 4 after sampling with 1 σ uncertainty of 6 %

^d The previous $\delta^{34}\text{S}(\text{OCS})$ value measured by Hattori et al. (2015) was (4.9 ± 0.3) ‰.



5 Figure 1: Schematic diagram of the OCS sampling system. System components: V, valve; pump, vacuum pump; MFC, mass flow controller.

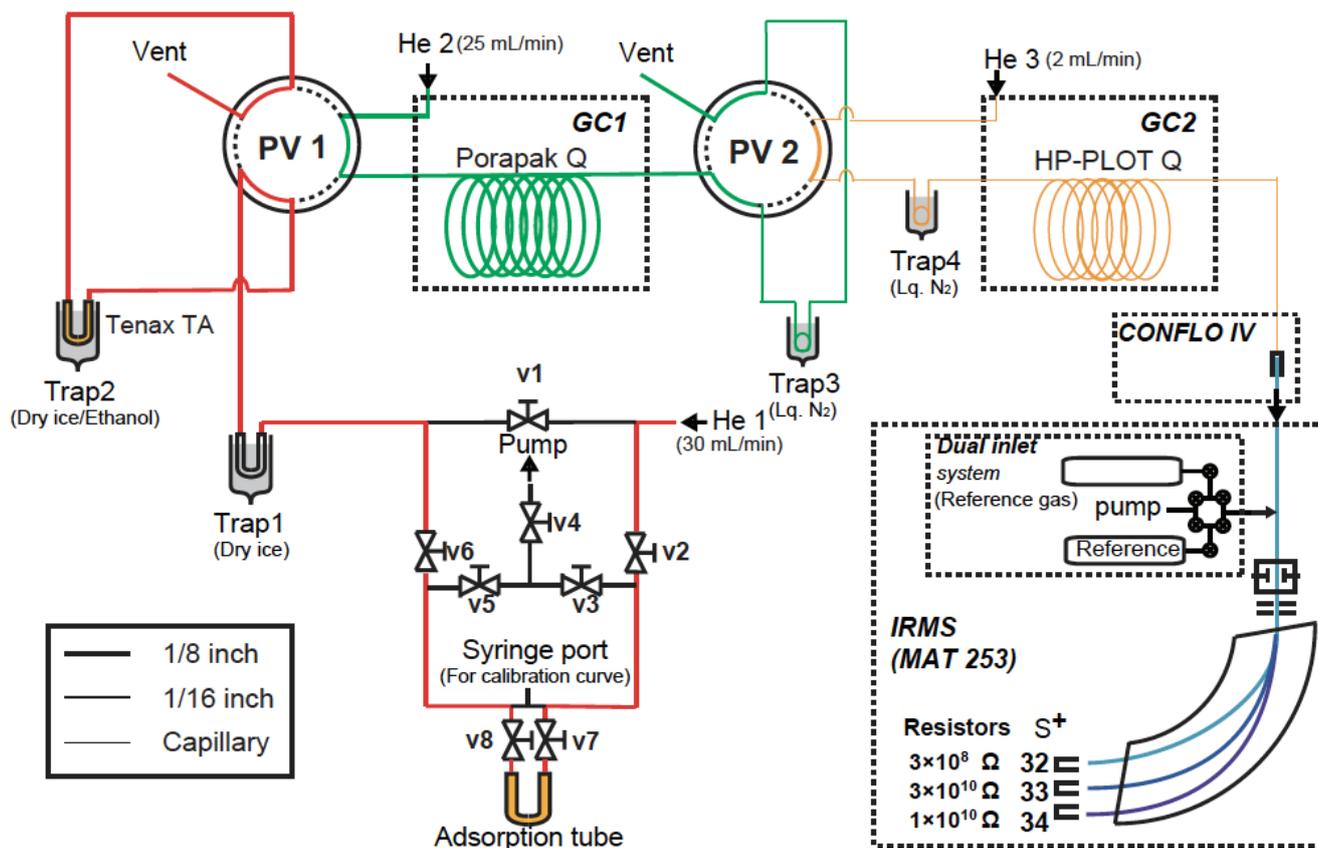
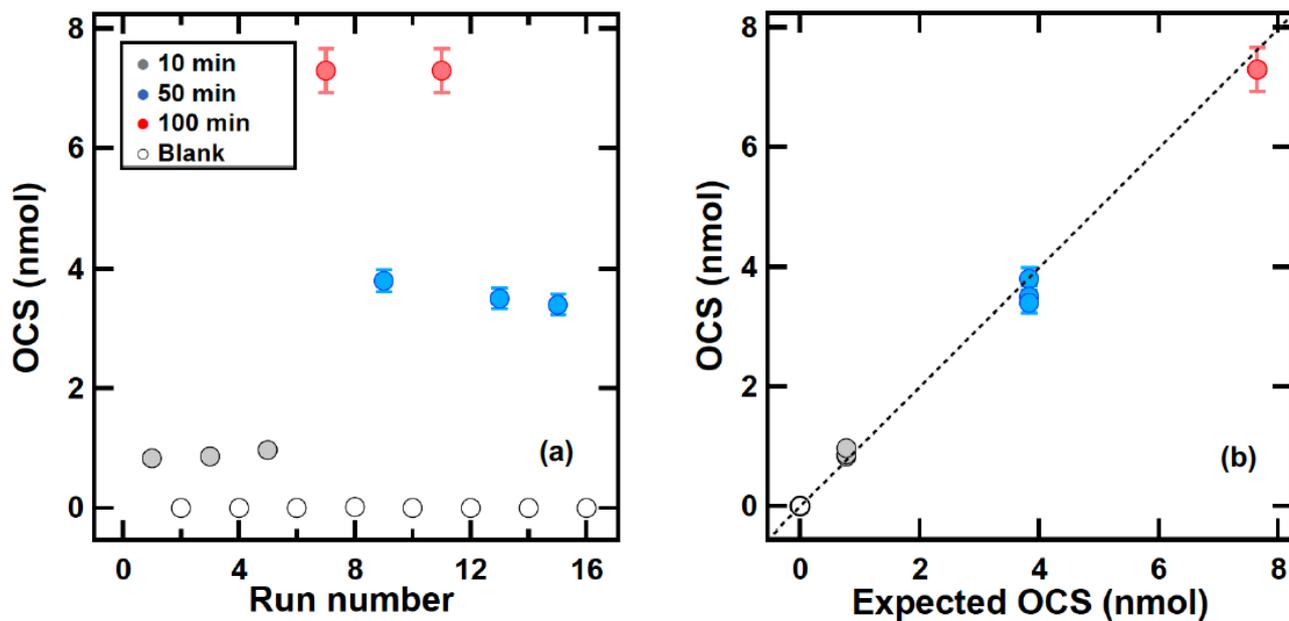


Figure 2: Schematic diagram of the OCS purification system. System components: V, valve; pump, vacuum pump; MFC, mass flow controller.

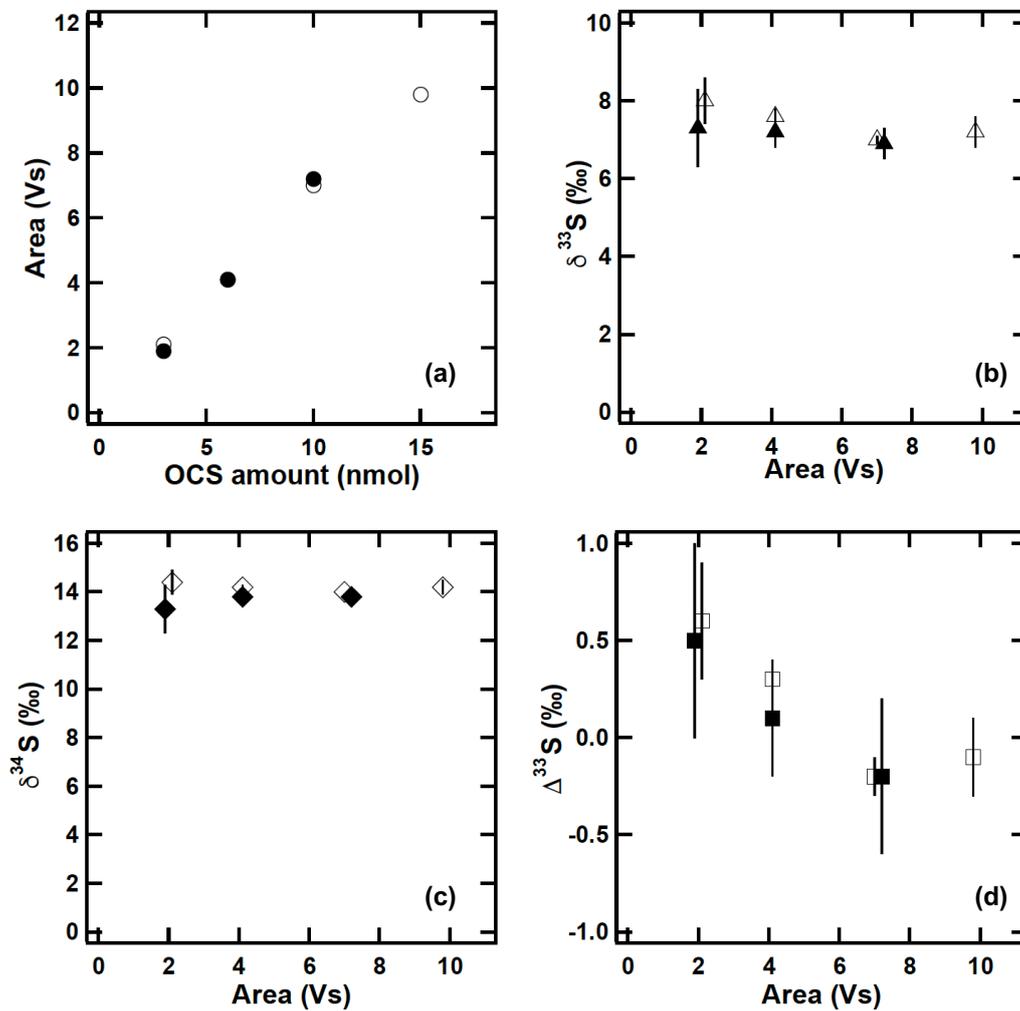
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Figure 3: OCS sampling using the sample F of (380 ± 15) pmol mol^{-1} with different sampling times of blank (0 min), 10 min, 50 min, and 100 min. (a) Collected OCS amounts as a function of run numbers. (b) Observed OCS amounts and OCS amounts calculated using OCS concentration multiplied by the sampling time. Error bar shows $\pm 3\%$ based on the residual of measured OCS peak area and calibrated OCS peak area. Dotted line shows the slope of $x=y$.

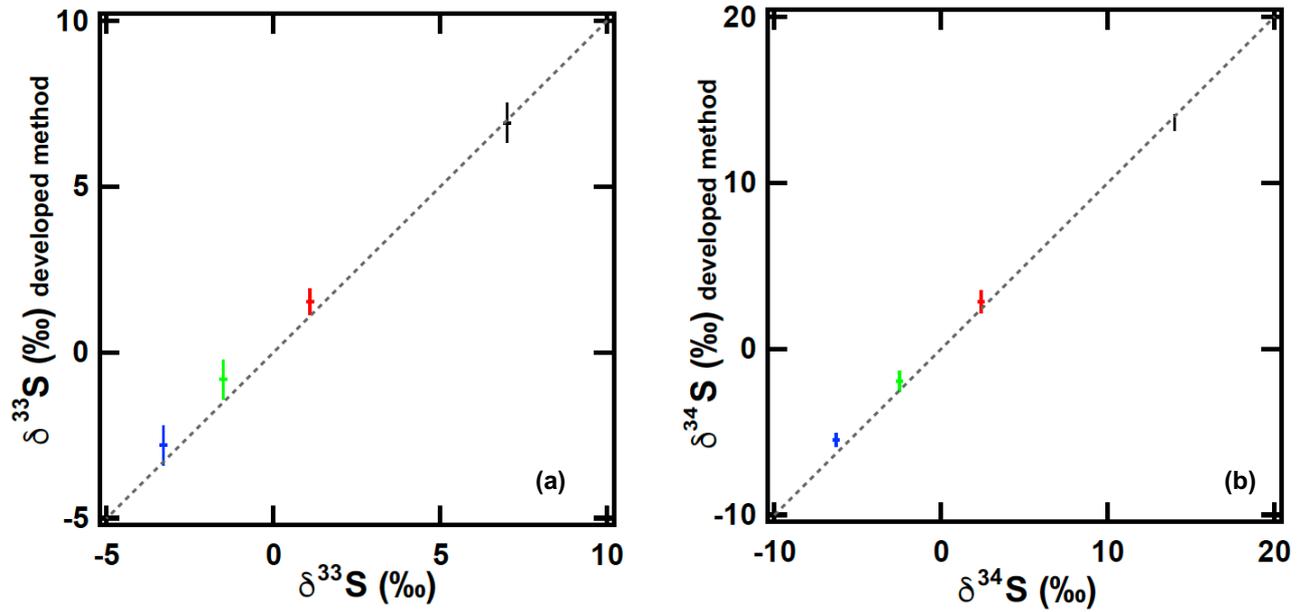
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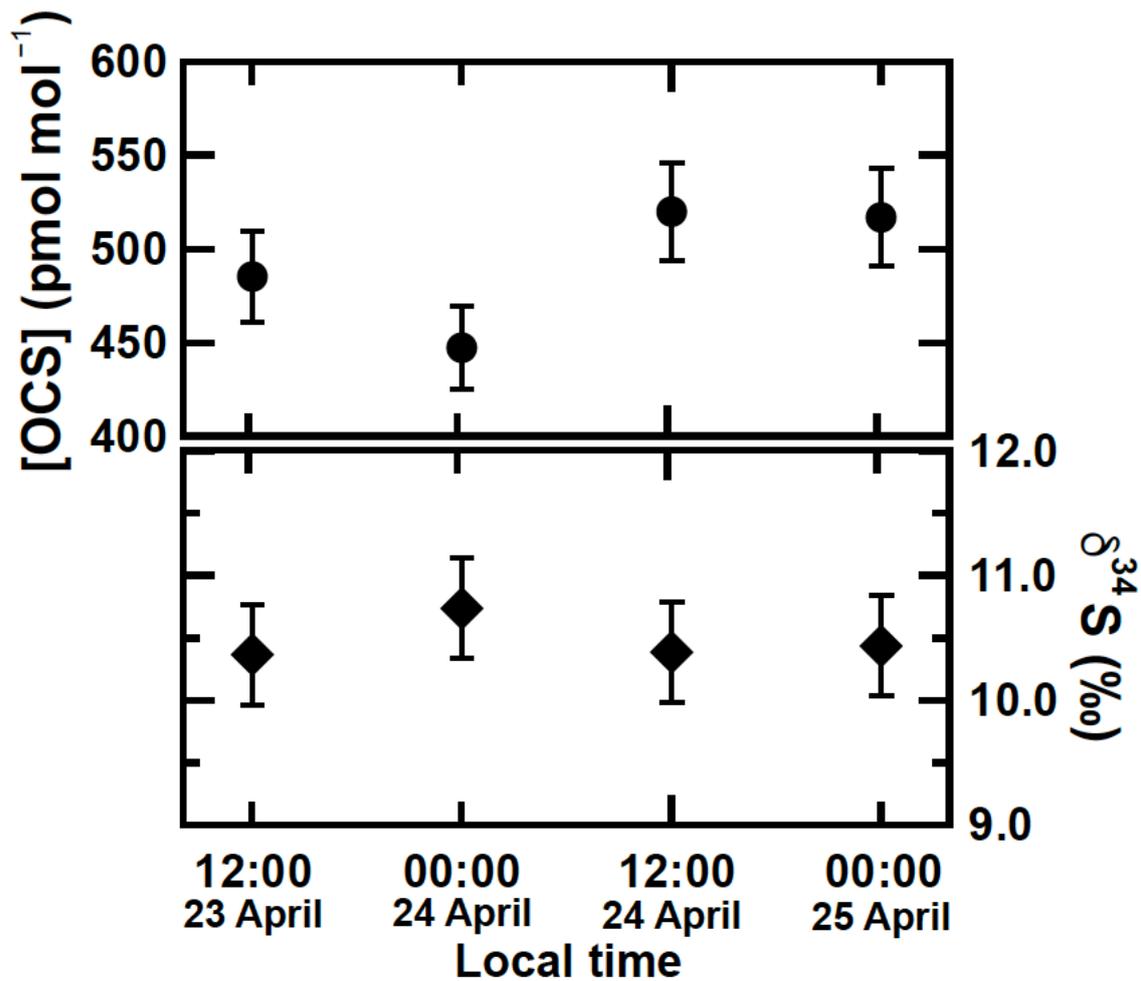
Figure 4: OCS amounts and sulfur isotope ratios of different amounts of OCS injections ascertained using the developed sampling/purification system and conventional syringe injection system (Hattori et al., 2015): (a) OCS amount; (b) $\delta^{33}\text{S}$; (c) $\delta^{34}\text{S}$; (d) $\Delta^{33}\text{S}$; closed symbols, sampling/purification system developed for this study; open symbols, conventional syringe injection system. All sulfur isotope ratios are relative to VCDT. The error bars are 1σ of the measurements based on triplicated measurements.



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Figure 5: Sulfur **isotope ratios** ((a) $\delta^{33}\text{S}$ and (b) $\delta^{34}\text{S}$) ascertained from the developed sampling/purification system (y -axis) and conventional syringe injection system (Hattori et al., 2015) (x -axis). OCS sample amounts are 8 nmol. Different colors represent different samples: black, sample B; red, sample C; green, sample D; blue, sample E. Dotted line **shows** the slope $x = y$. The error bar is 1σ of each amount of triplicated OCS injection.

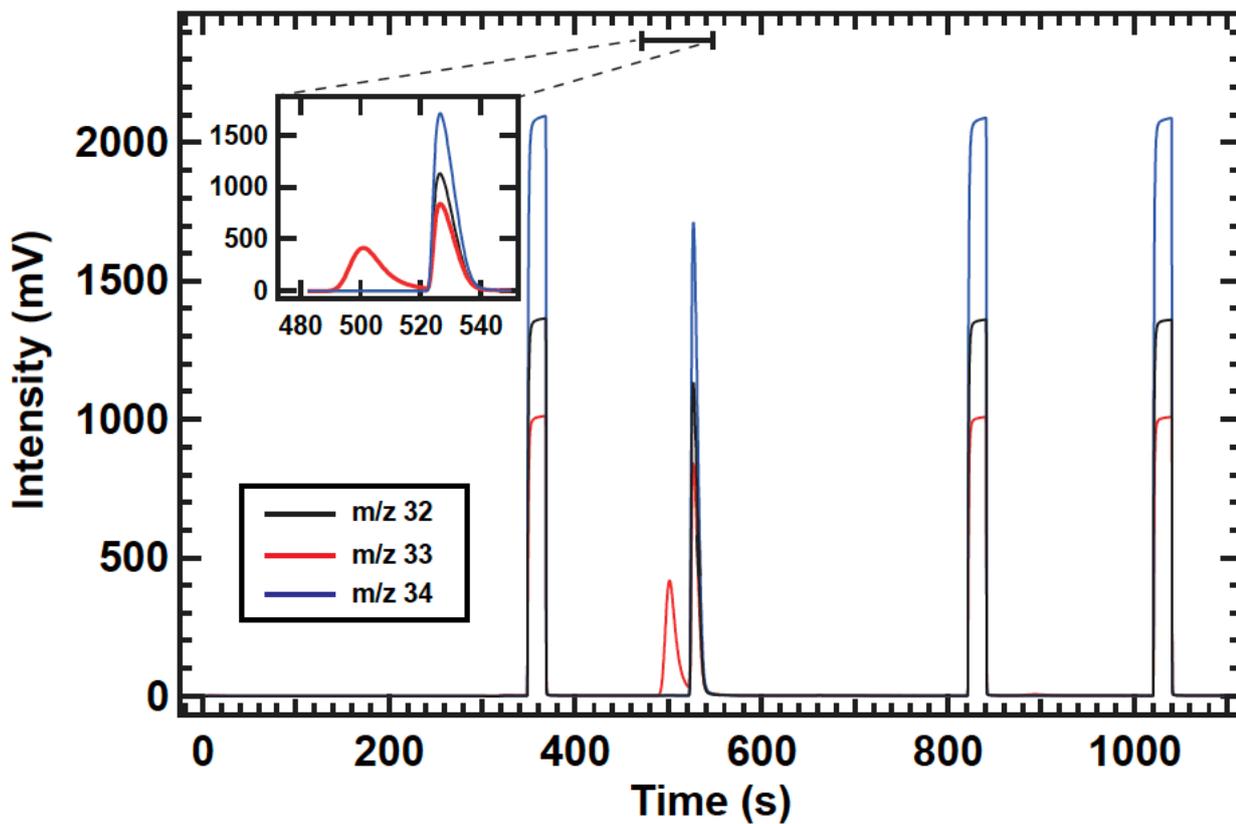
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Figure 6: OCS concentrations and $\delta^{34}\text{S}(\text{OCS})$ values for atmospheric samples collected at Suzukakedai campus of Tokyo Institute of Technology located in Yokohama, Japan. The error bar is 6 % for OCS concentration based on the precisions of syringe injection and flow rate of the diaphragm pump in the sampling system. The precision of $\delta^{34}\text{S}$

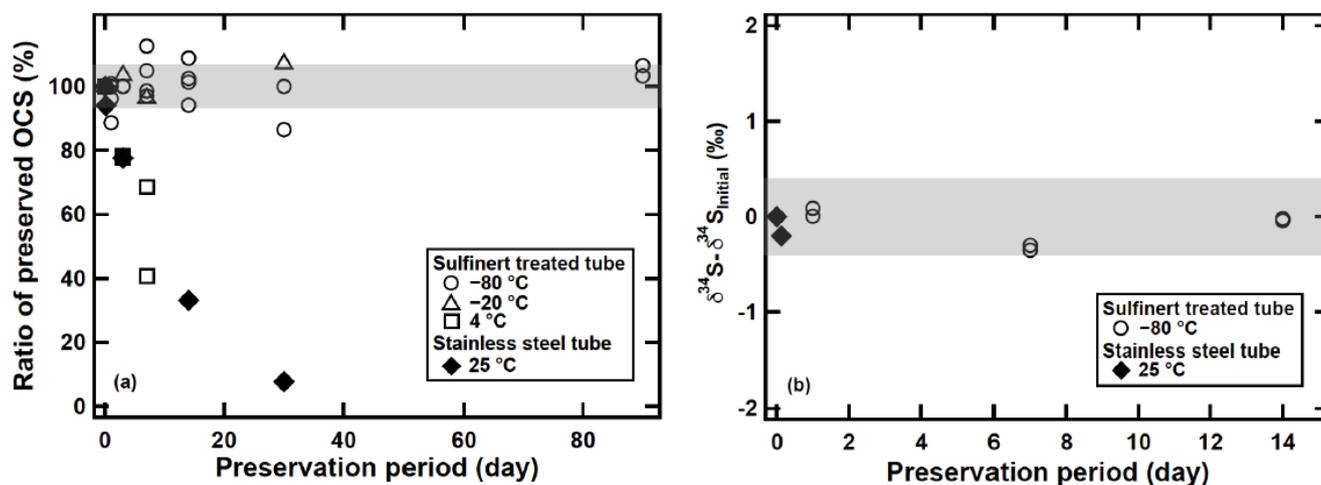
10 is estimated from 1σ uncertainty of 0.4 %.



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Figure 7: IR-MS chromatogram of atmospheric samples collected at the Suzukakedai campus of the Tokyo Institute of Technology. Liquid N₂ removal from trap 4 occurred at 0 s in the purification system. Reference OCS was injected three times starting at 350 s, 825 s, and 1025 s for 20 s.

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Figure 8: (a) Changes in OCS concentrations preserved in the OCS storage test in adsorption tubes at different temperatures and tubes. (b) Changes of $\delta^{34}\text{S}$ (OCS) preserved in the OCS storage test. The shaded bar shows $\pm 6\%$ for OCS concentration and $\pm 0.4\%$ for $\delta^{34}\text{S}$ (OCS) value based on the precisions of syringe injection and the flow rate of the diaphragm pump in the sampling system.

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