

EGU21-2214

Isotopic constraints on the tropospheric carbonyl sulfide budget

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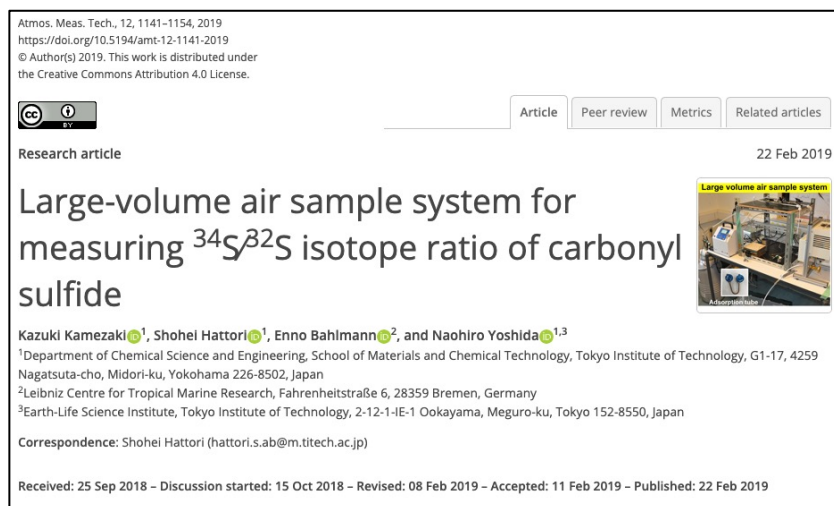
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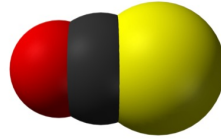


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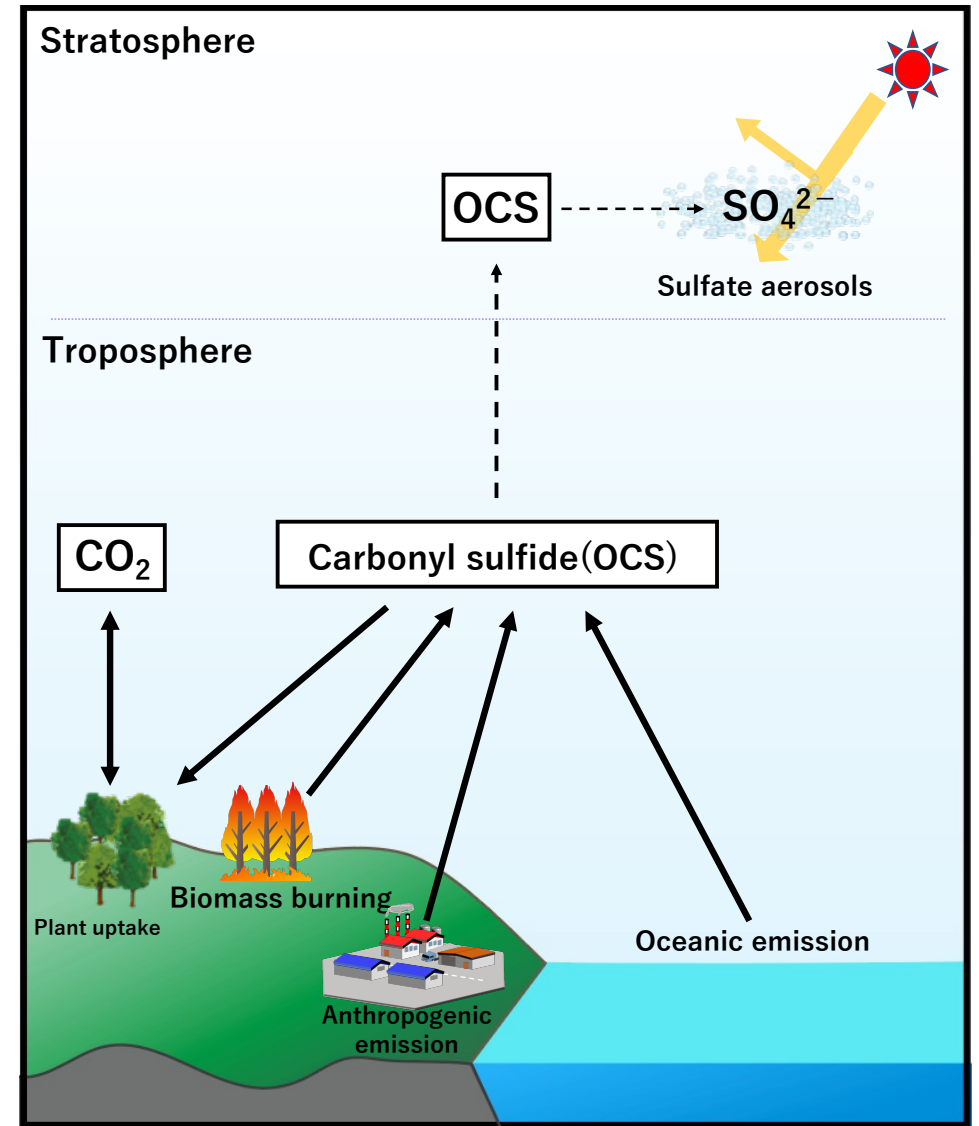


<https://doi.org/10.1073/pnas.2007260117>

Carbonyl sulfide (OCS)



- A proxy for photosynthesis rate because OCS is consumed by plant leaves together with assimilation of CO_2 , but leaves do not emit OCS to the atmosphere by respiration
- Indirectly affecting Earth's radiation balance by becoming main sulfur source of stratospheric sulfate aerosol



The atmospheric OCS budget

Bottom-up approach

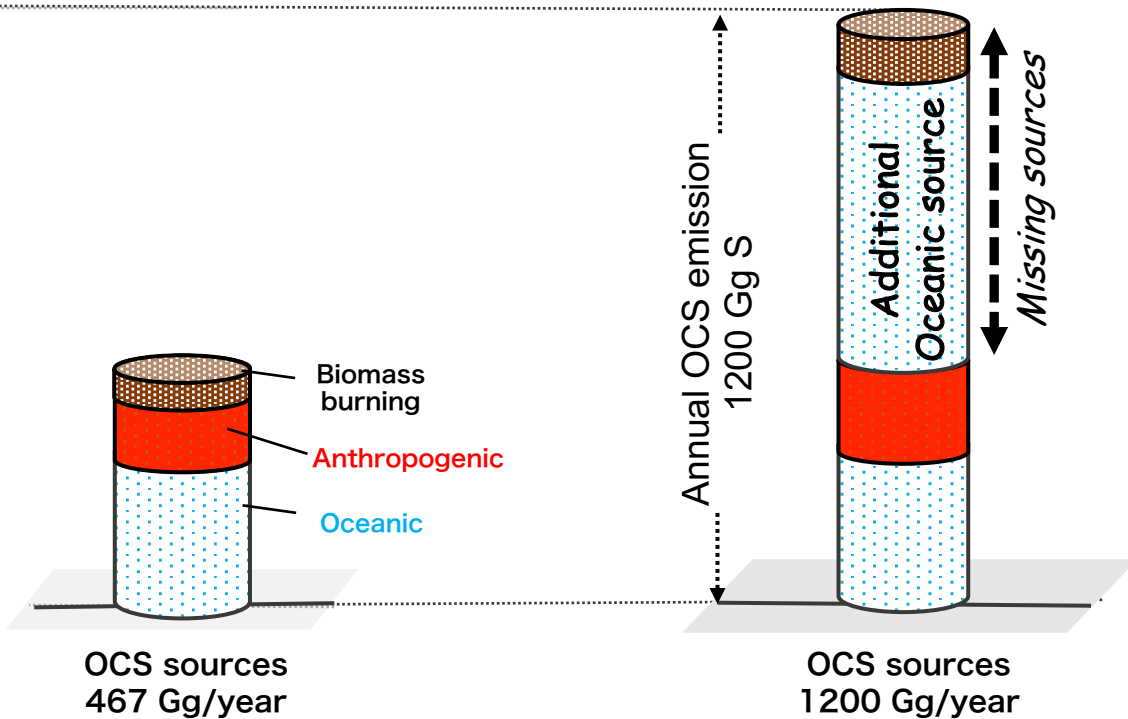
Top-down approach

Whereas the OCS budget has been regarded as closed in an earlier study reported by Kettle et al. (2002), upward revision of the vegetation OCS sink has led to a missing OCS source of 230 to 800 Gg S y^{-1} .

Berry et al. (2013) first proposed the oceanic OCS source to balance the budget residual.

By contrast, Lennartz et al. (2017) inferred that oceanic OCS emission is too low to account for the missing OCS source.

Recently, Zumkher et al. (2018) showed that anthropogenic OCS source is roughly corresponds to the estimate of the missing OCS source using global gridded inventory.



Kettle et al. (2002)

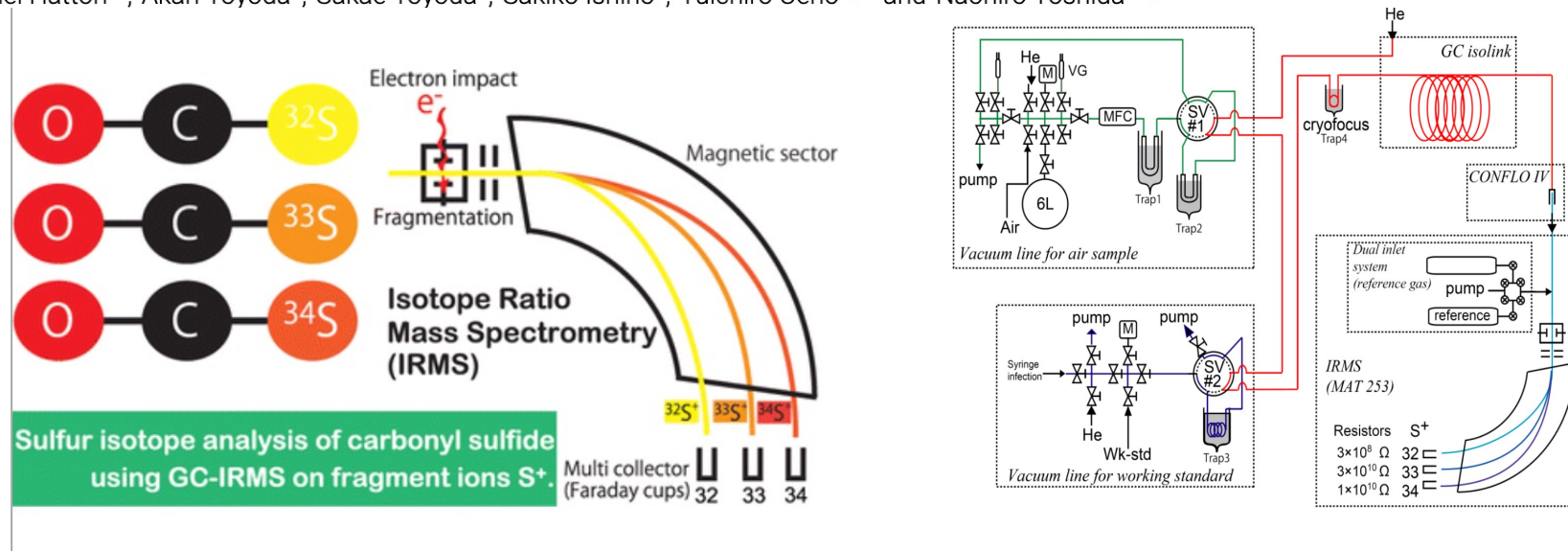
Berry et al. (2013)

The lack of observational evidence has led to continuous debate whether the missing OCS source is oceanic emission or anthropogenic emission.

Sulfur isotope measurement of OCS

Determination of the Sulfur Isotope Ratio in Carbonyl Sulfide Using Gas Chromatography/Isotope Ratio Mass Spectrometry on Fragment Ions $^{32}\text{S}^+$, $^{33}\text{S}^+$, and $^{34}\text{S}^+$

Shohei Hattori^{*†}, Akari Toyoda[‡], Sakae Toyoda[‡], Sakiko Ishino[†], Yuichiro Ueno^{†§} and Naohiro Yoshida^{†‡§}

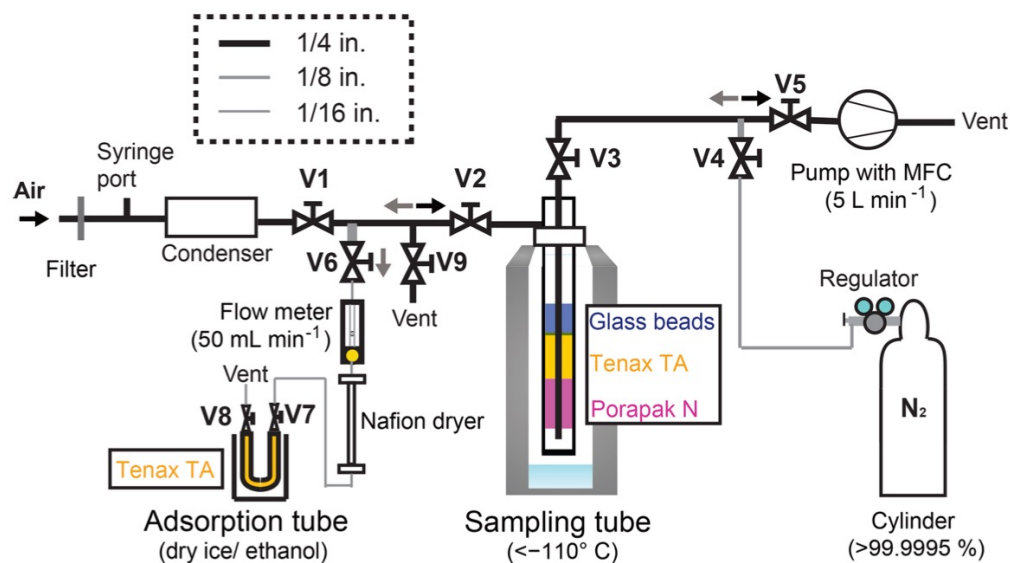


Hattori et al. 2015

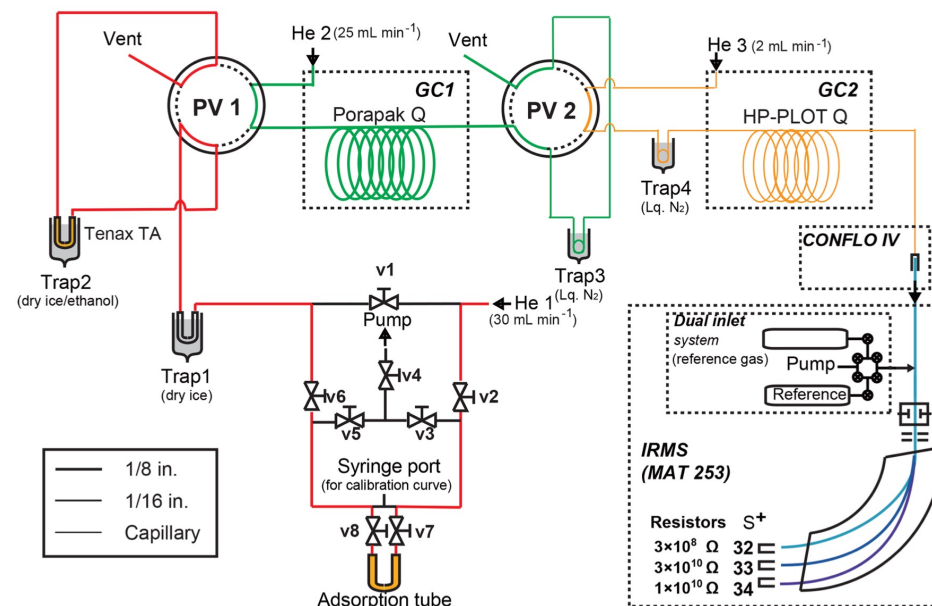
This S^+ fragmentation method requires hundreds of liters of air to obtain nanomoles of OCS

Extension of S⁺ method to atmospheric OCS

■ Sampling system



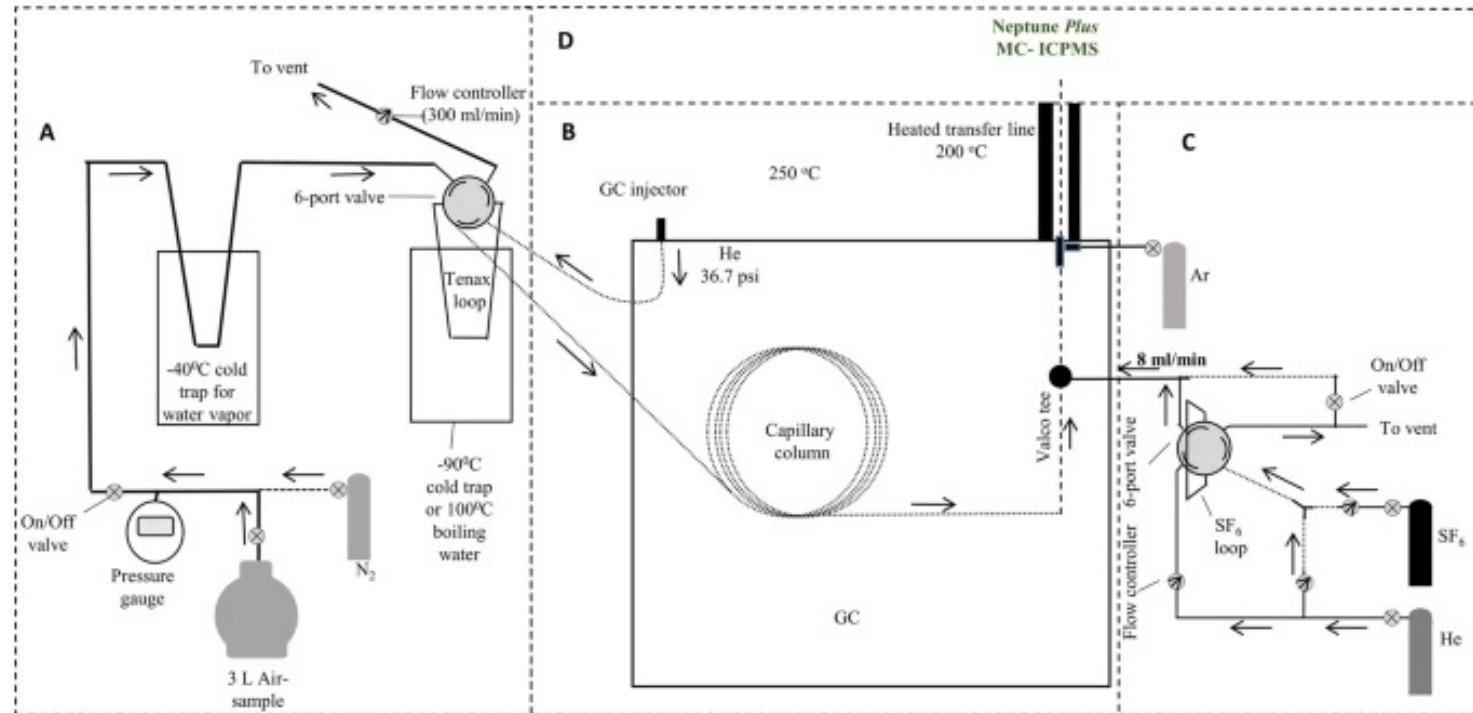
■ Purification system



Kamezaki et al. (2019)

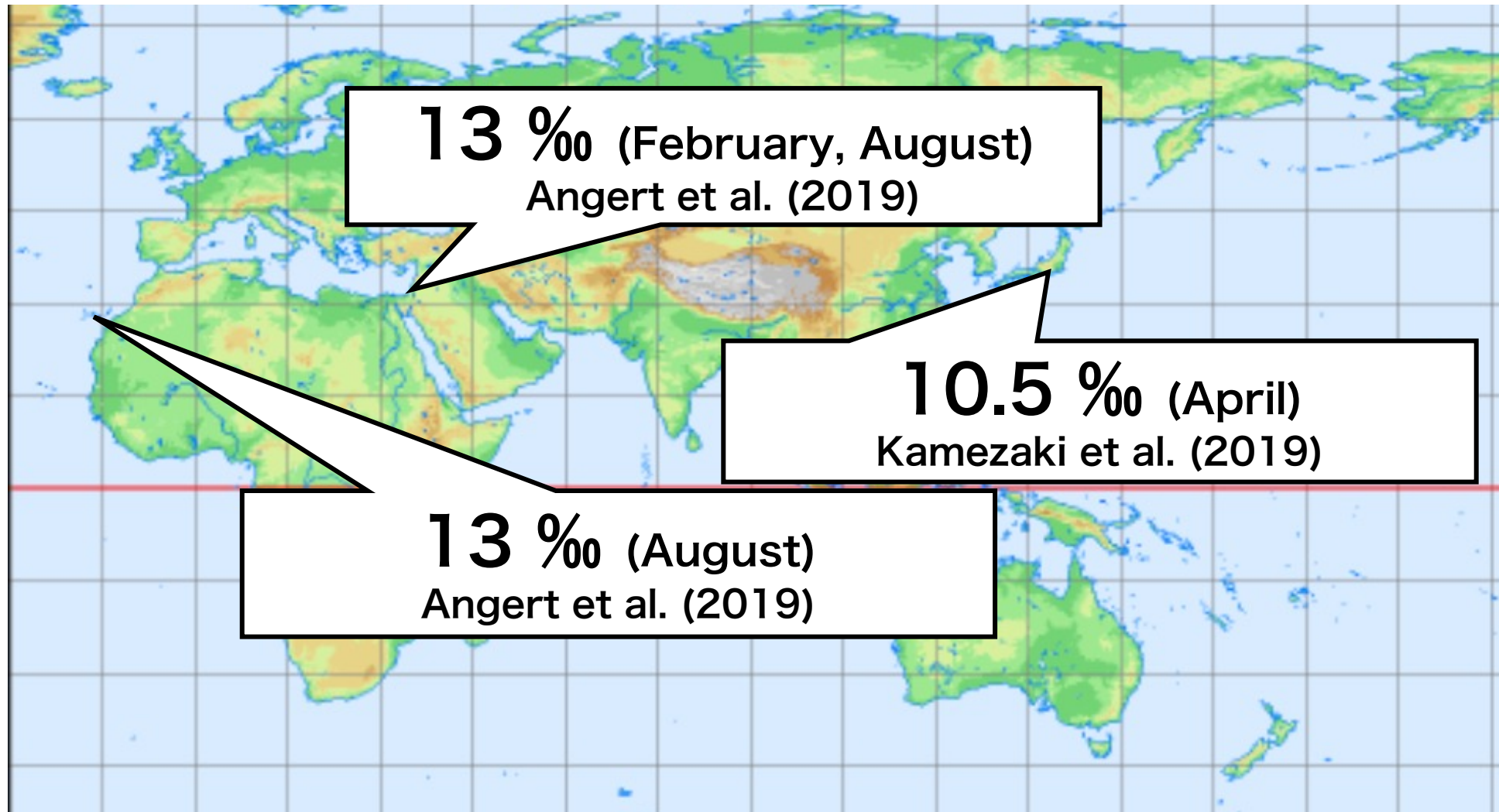
Development of a high-volume air sampling system coupled with GC-IRMS method has enabled observation of the atmospheric $\delta^{34}\text{S}(\text{OCS})$ and the value of $\delta^{34}\text{S}(\text{OCS})$ of $(10.5 \pm 0.4)\text{‰}$ was reported for April 2018 at Yokohama, Japan.

Atmospheric $\delta^{34}\text{S}(\text{OCS})$ measurement by GC-MC-ICPMS



Angert et al. (2019)

Angert et al. (2019) developed the $\delta^{34}\text{S}(\text{OCS})$ measurement method using GC-MCIRMS. Based on the similarity of atmospheric $\delta^{34}\text{S}(\text{OCS})$ at two sites (Israel and the Canary Islands), with values of 12.8 to 13.4‰ reported sulfur isotopic homogeneity of atmospheric OCS by Angert et al. (2019)

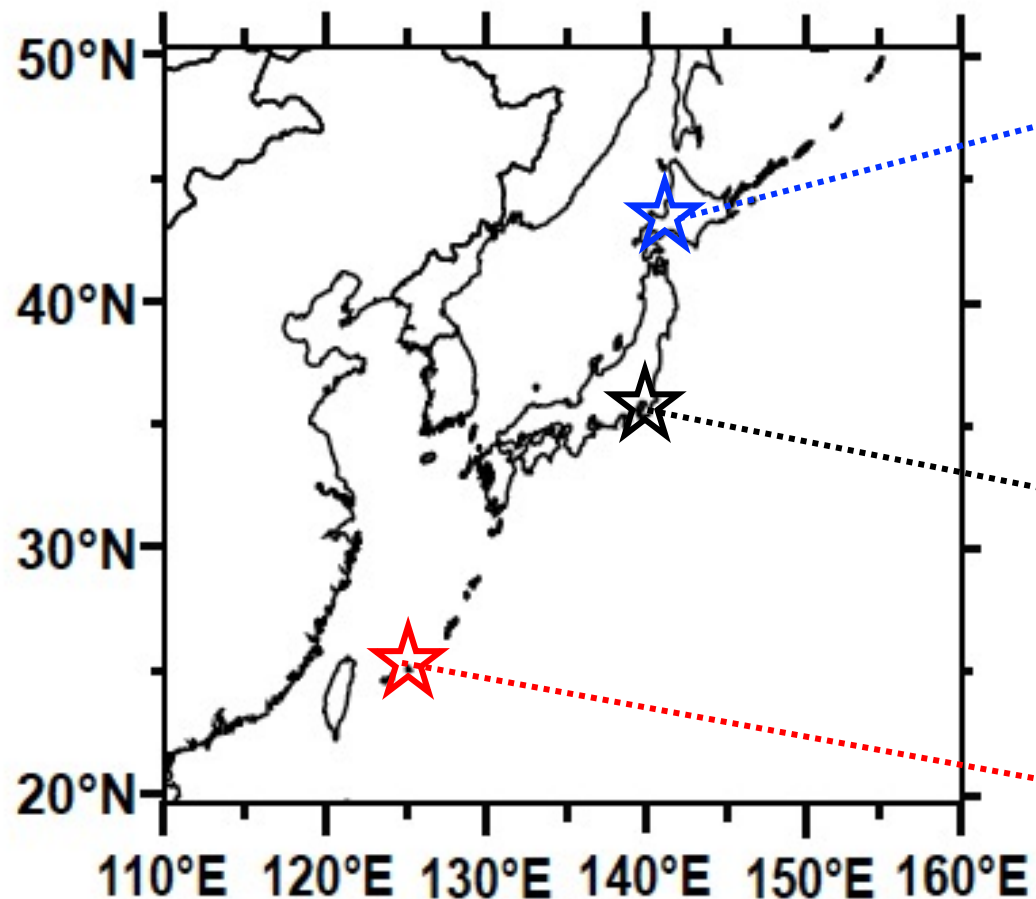


Atmospheric $\delta^{34}\text{S}(\text{OCS})$ also varies might caused by geographic effect

$\delta^{34}\text{S}(\text{OCS})$ potentially valuable information about its sources and sinks

Methods: Sites, sampling

■ Sites



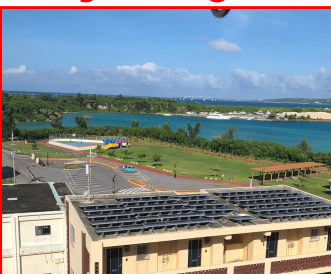
Otaru



Yokohama



Miyakojima



■ Sampling

OCS were collected at three locations on the following schedule

1. February to March 2019
2. July to August 2020
3. February to March 2020

OCS was concentrated from over 150 L using sampling system and the collected OCS was stored at -80°C until measurement to prevent alteration of OCS

■ Back-Trajectory Analysis

(NOAA HYSPLIT and TrajStat software)

- Five-days
- 00:00 and 12:00
- half the height of the PBL

Results: Backward trajectory analysis, OCS concentration and $\delta^{34}\text{S}$ value

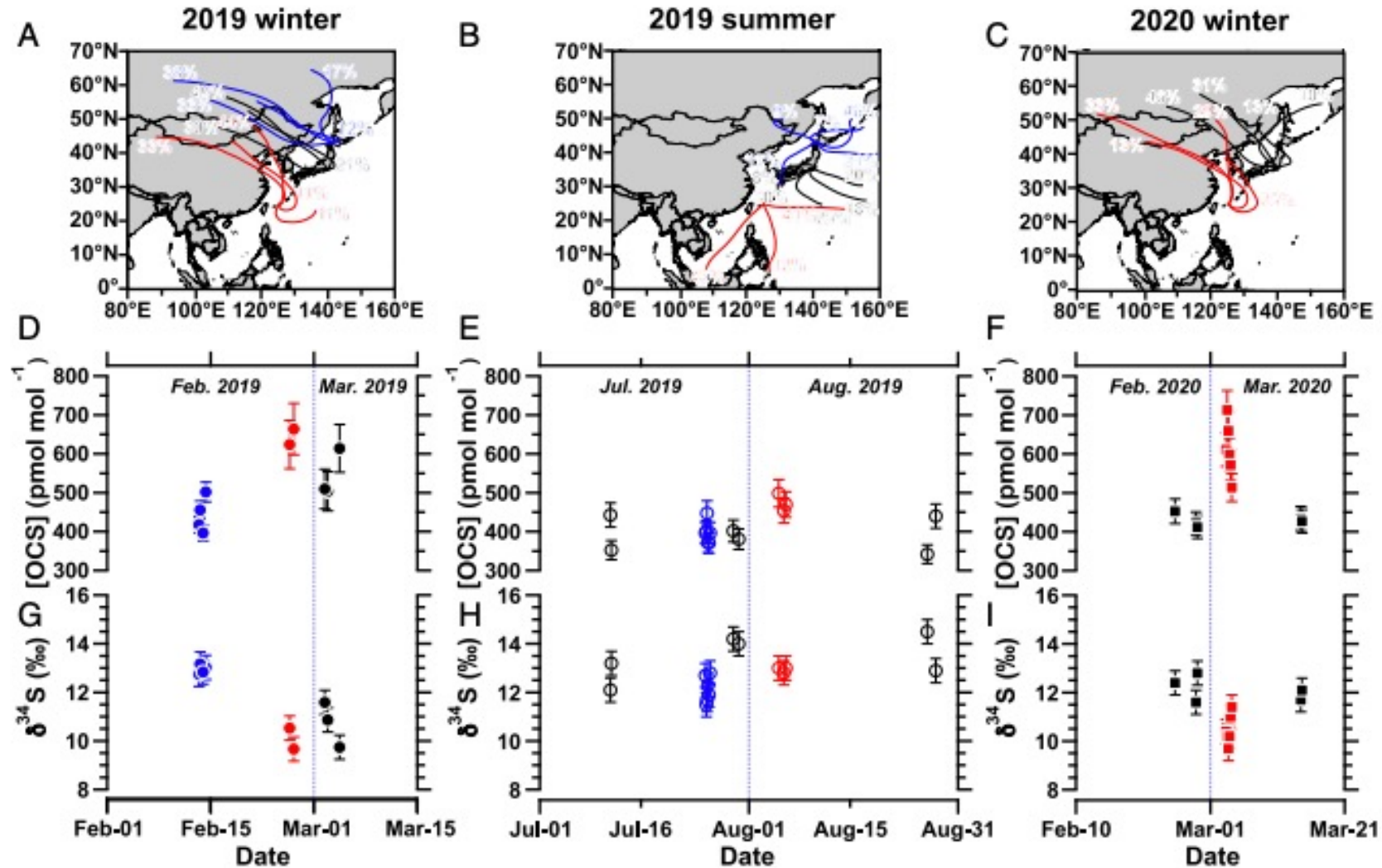
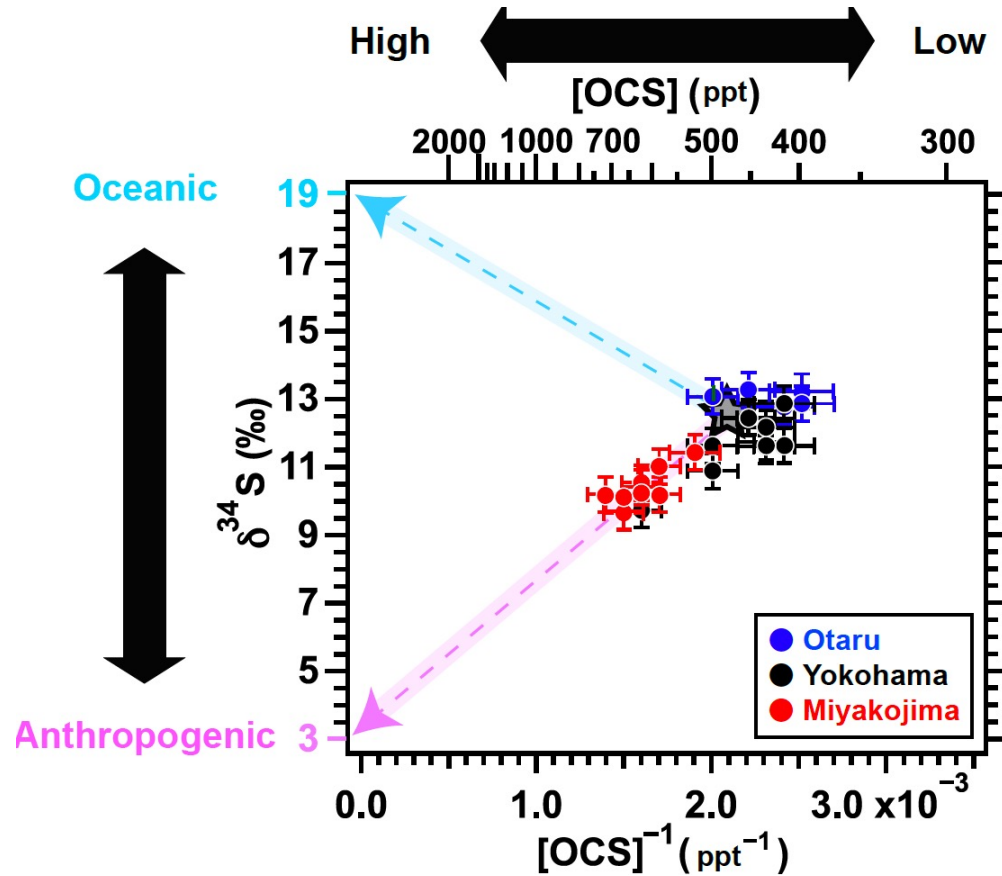


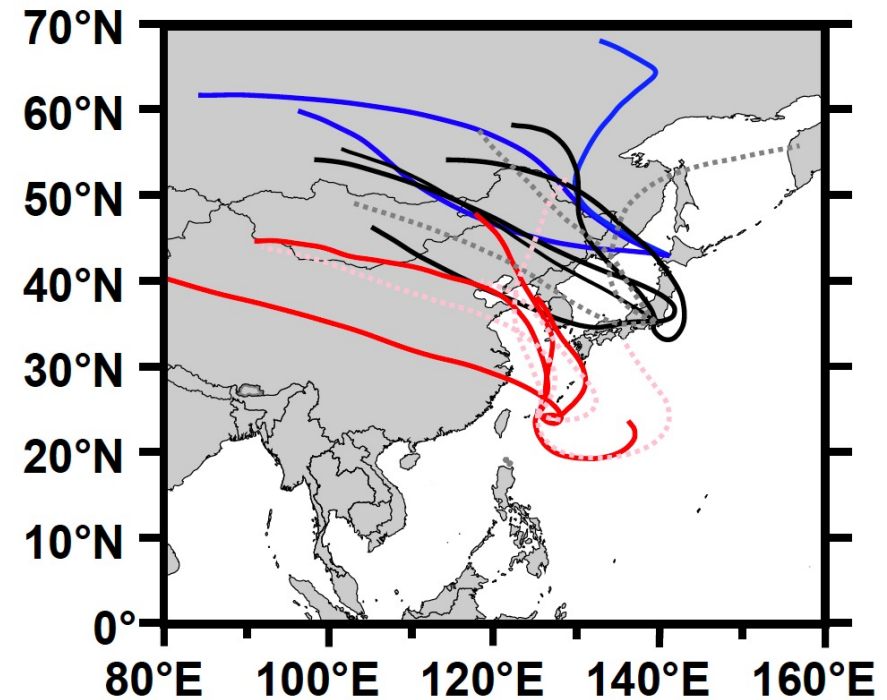
Fig. 1. Back trajectory analysis for three Japanese sites for (A) 2019 winter, (B) 2019 summer, and (C) 2020 winter. The time series of (D–F) [OCS] and (G–I) $\delta^{34}\text{S}$ (OCS) during this study period. Red lines and plots represent data for Miyakojima. Black lines and plots represent data for Yokohama. Blue lines and plots represent data for Otaru.

Discussion : Geographic effect

■ Keeling plot approach

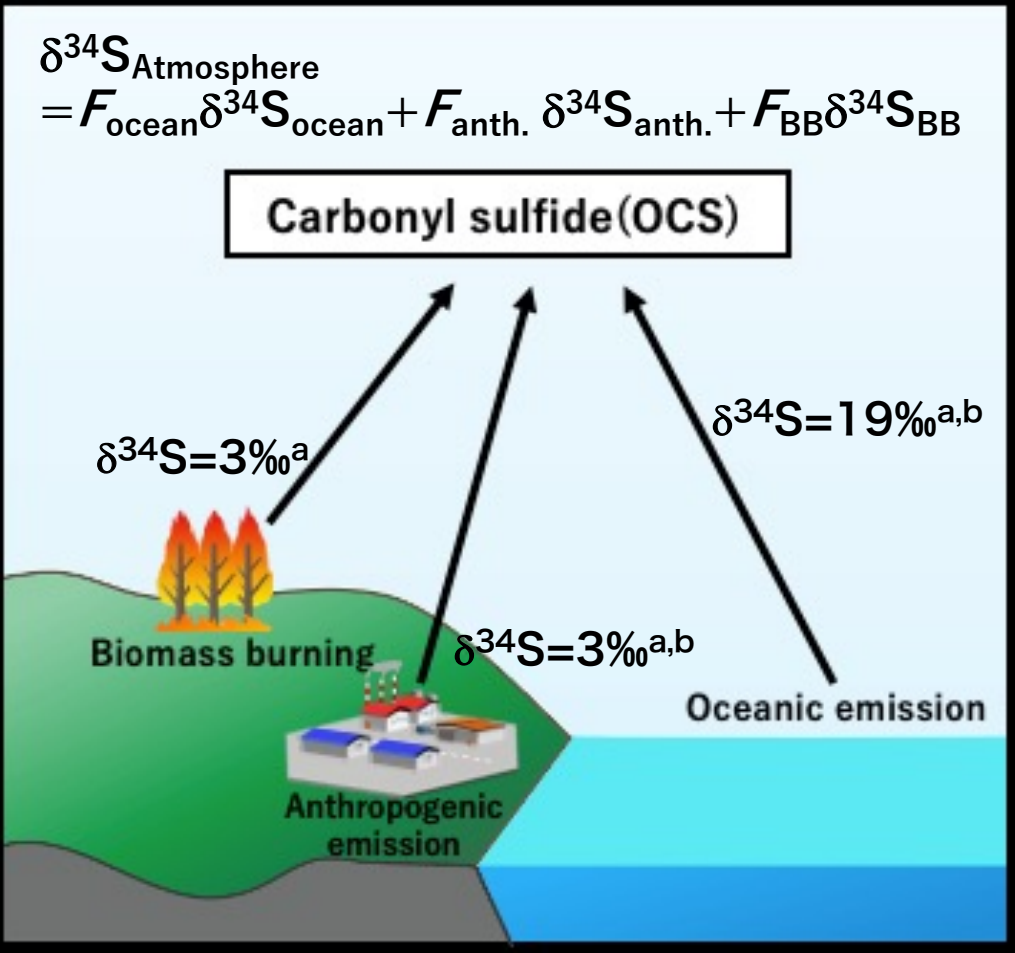


■ Backward trajectory analysis



The contribution of anthropogenic OCS caused the north–south gradients in eastern Asia in winter
The background $\delta^{34}\text{S}(\text{OCS})$ value were within the range of 12.0 to 13.5‰

Discussion : Sulfur isotopic constraints for the atmospheric OCS budget



^aNewman et al. (1990); ^bAngert et al. (2019)

OCS source	Kettle et al. (2002)	Scenarios considering the missing OCS source			
		Oceanic enhancement	Anthropogenic enhancement		
			Average	Max.	Min.
Ocean (direct)	39	39	39	39	39
Ocean (indirect)	237	237	237	237	237
Additional oceanic flux	—	600*	450	270	633
Anthropogenic	180	180	406 [†]	586 [†]	223 [†]
Biomass burning	11	136*	60 [‡]	60 [‡]	60 [‡]
$\delta^{34}\text{S}(\text{OCS}) (\text{‰})$	12.5	14.8	12.7	10.3	15.2

Unit for OCS is Gg S y⁻¹
 *Estimated by Berry et al. (2013)
 †Estimated by Zumkehr et al. (2018)
 ‡Estimated by Stinecipher et al. (2019)

Anthropogenic enhancement scenario considering updated OCS emissions from anthropogenic sources ranging from 223 to 586 GgS y⁻¹ and from biomass burning with 60 GgS y⁻¹.

In the anthropogenic enhancement scenario, we also added additional oceanic OCS emission ranging from 270 to 633 GgS y⁻¹ to make an equivalent of OCS sources with the oceanic enhancement scenario

Conclusions

We developed a new OCS sampling and purification system and we demonstrated variation of $\delta^{34}\text{S}(\text{OCS})$ of 9.7 to 14.5‰ in Japan.

Most notably, the north–south latitudinal gradient of $\delta^{34}\text{S}(\text{OCS})$ during winter is evidence of a very substantial emission of OCS from the Asian continent that is transported to the Western Pacific by outflow from the Asian monsoon.

The sulfur isotopic mass balance revealed that anthropogenic OCS emission of 350 to 462 GgS y⁻¹ and oceanic enhancement with 394 to 506 GgS y⁻¹ are likely to explain the range of background $\delta^{34}\text{S}(\text{OCS})$, bridging the knowledge gap of the atmospheric OCS budget.

This sulfur isotopic constraint on atmospheric OCS is an important step, but more observations, together with isotopic characterizations and analysis using a chemical transport model, will enable detailed quantitative conclusions. The increased importance of anthropogenic OCS emission at midlow latitudes has important implications for anthropogenic climate change and stratospheric chemistry in the past and futures.

Acknowledgements

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

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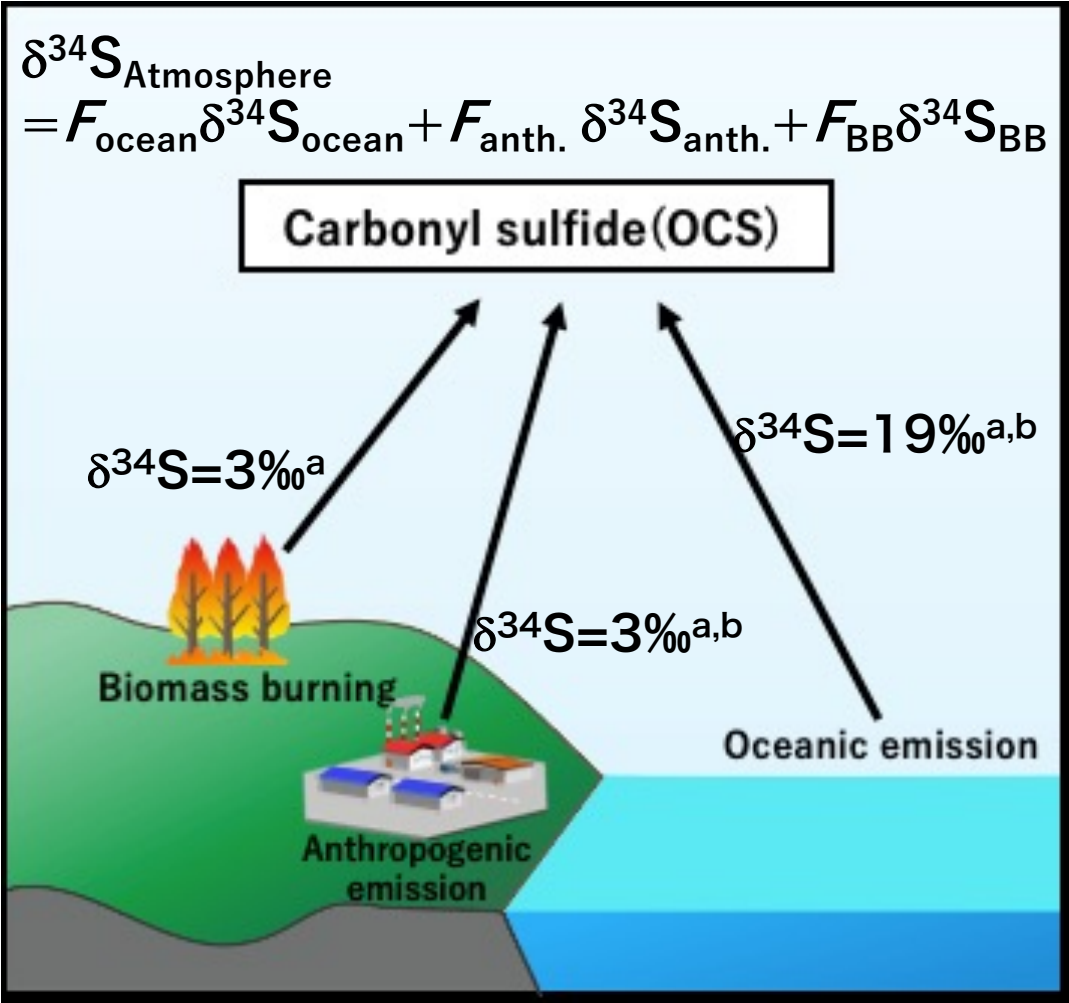
Constraining the atmospheric OCS budget from sulfur isotopes

Shohei Hattori, Kazuki Kamezaki, and Naohiro Yoshida
[+ See all authors and affiliations](#)

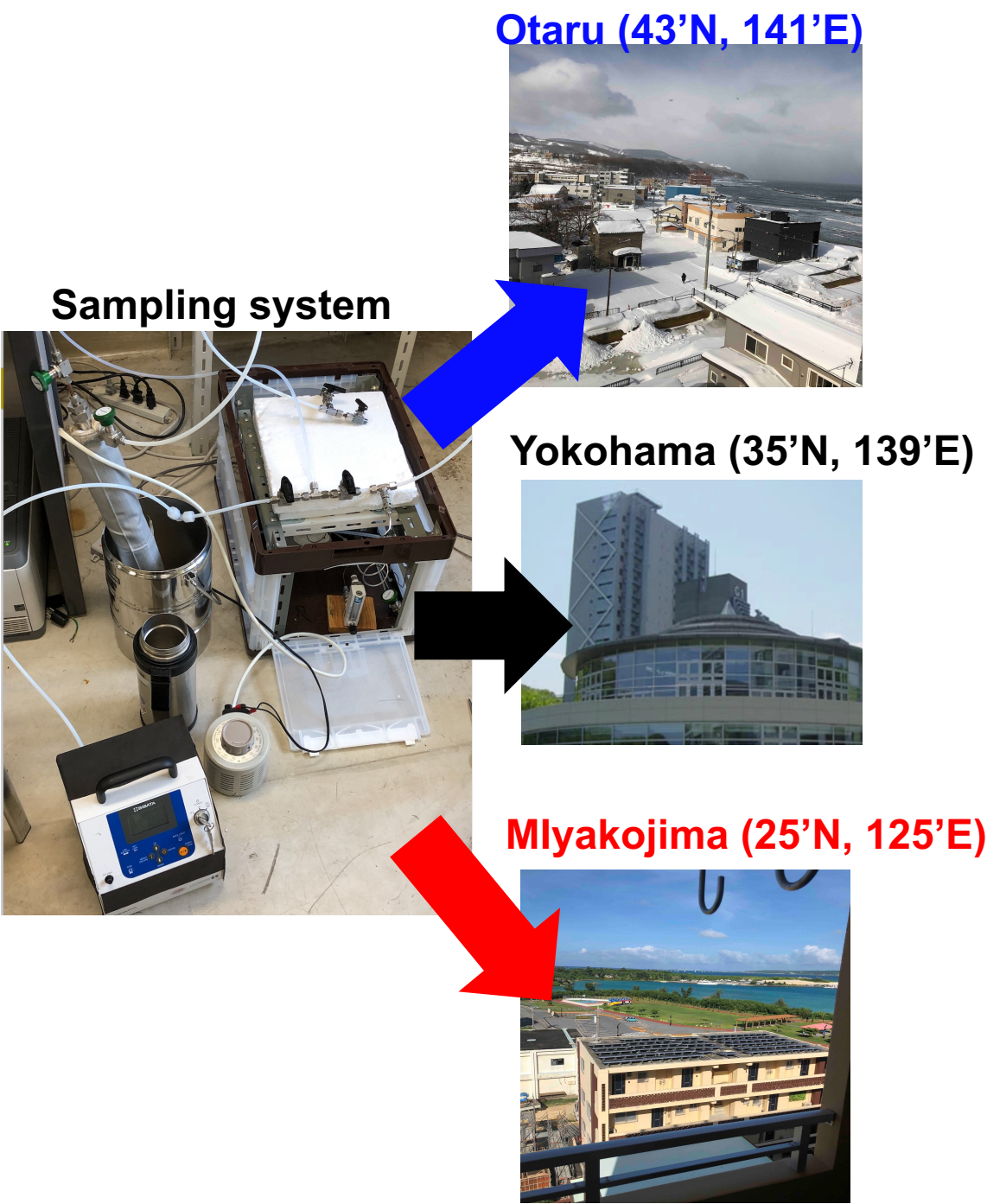
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For two minutes presentation

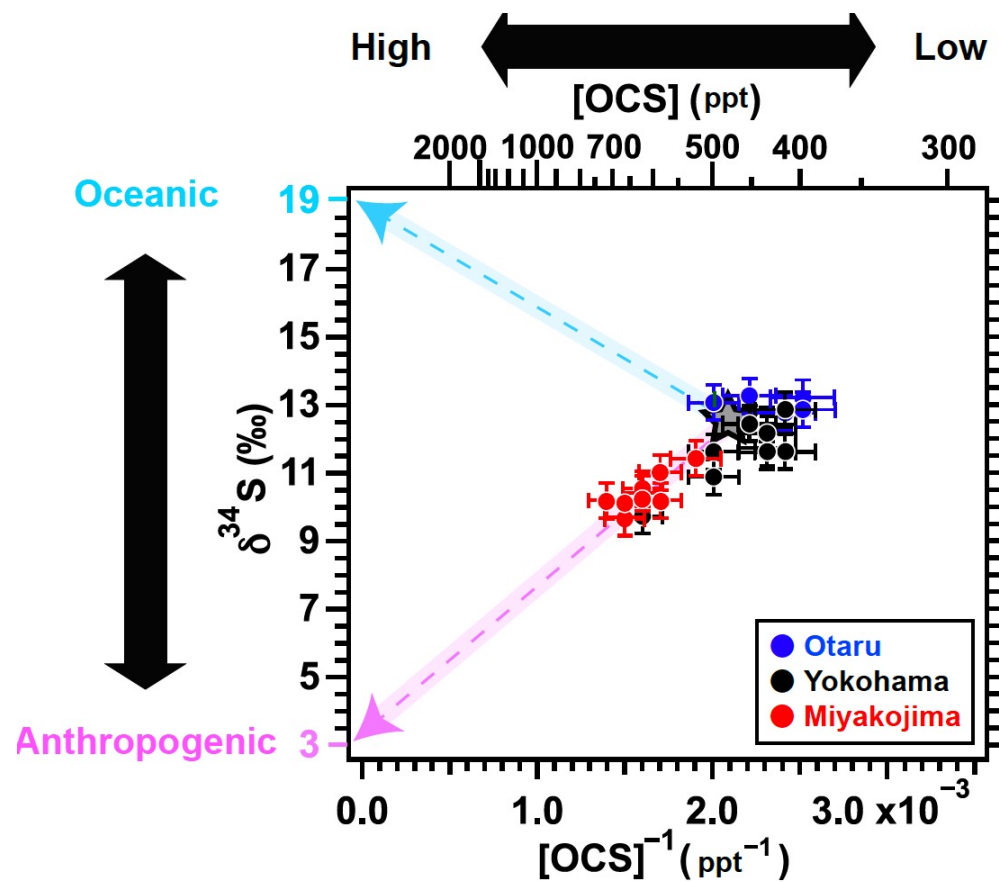


^aNewman et al. (1990); ^bAngert et al. (2019)

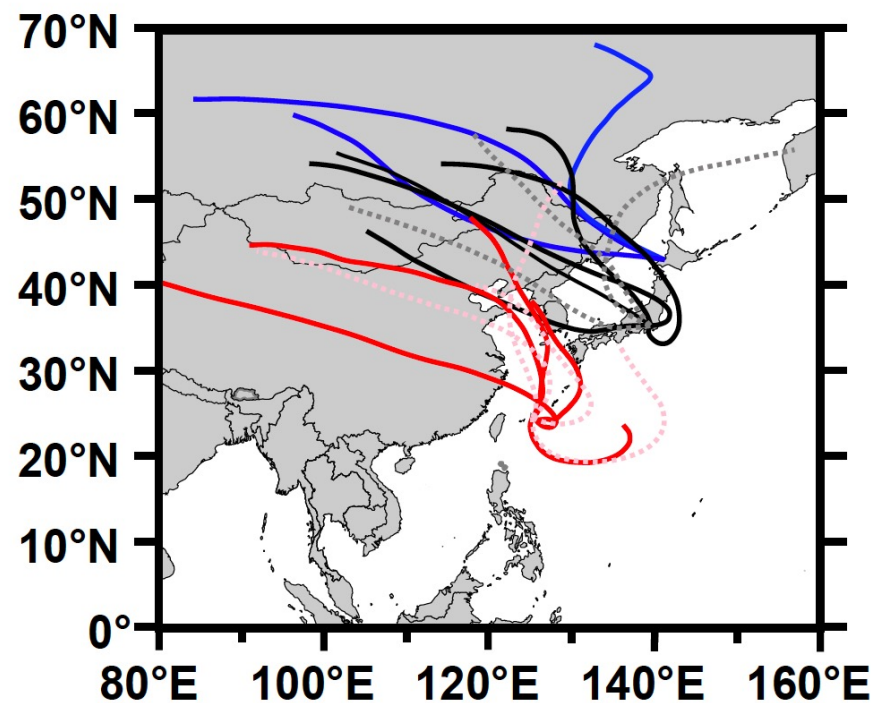


For two minutes presentation

Keeling plot approach



Backward trajectory analysis



Origin of missing OCS source?

