



Global measurements of atmospheric carbonyl sulfide (OCS), OC³⁴S and O¹³CS

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ABSTRACT

Near global 85° S–85° N atmospheric measurement of carbonyl sulfide (OCS), including the minor OC³⁴S and O¹³CS isotopologues, were made by the Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS) in low Earth orbit. ACE-FTS data provide volume mixing ratio (VMR) profiles of OCS, OC³⁴S and O¹³CS from 8 km in troposphere up to 31 km in the stratosphere. The global zonal and seasonal distributions of OCS isotopologues were studied. OCS observations made with the MkIV balloon-borne Fourier transform spectrometer (FTS) are also presented. The results indicate a slight enrichment of OC³⁴S and a significant enrichment of O¹³CS as the altitude increases. The contribution of OCS to the background Stratospheric Sulfate Aerosol Layer (SSA) is discussed and ACE-FTS data indicate that OCS is a major contributor.

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1. Introduction

Carbonyl sulfide (OCS) is the most abundant sulfur-containing gas in the atmosphere. The OCS distribution, sources and sinks have been studied in the troposphere [1–3]. The main source of OCS is biogenic activity either from direct emission or indirectly by oxidation of CS₂ and dimethyl sulfide (DMS). Biomass burning [4], soil and wetland emissions [2] are additional biogenic sources of OCS.

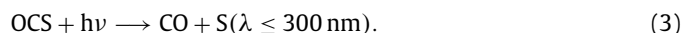
OCS is also emitted by anthropogenic activities, particularly by oxidation of CS₂ that is released by industry. Uptake by vegetation and soil are the major tropospheric sinks of OCS. The destruction of OCS by plants can be used to study the carbon cycle in the troposphere [3]. OCS assimilation by plants is assumed to be similar to the photosynthetic uptake of CO₂ but is irreversible [3].

The total OCS atmospheric lifetime is estimated to be 2.5 years [5]. Due to its low reactivity and relatively long lifetime, OCS is the only sulfur containing gas that can reach the stratosphere except following major volcanic eruptions during which SO₂ is directly injected into the stratosphere. In the stratosphere, OCS is destroyed

by reaction with OH or O radicals,



However, the main sink of OCS in the stratosphere is via photolysis [6–8],



Danielache et al. [9] calculate that reaction (1) with OH dominates in the troposphere, reaction (2) with O is responsible for 20% of OCS destruction in the stratosphere and photolysis (3) at 80% dominates in the stratosphere. The stratospheric lifetime of OCS mainly due to photolysis, is estimated to be 64 years [10].

The sulfur products produced from the above reactions (SH, SO and S) are rapidly oxidized in the stratosphere to SO₂. SO₂ is converted to sulfate aerosol by reaction with OH, so OCS is a precursor to stratospheric sulfate aerosol (SSA) [7]. SSA is an optically thin layer of sulfuric acid droplets that extends from the tropopause upwards into the stratosphere, also called the Junge layer. SSA reportedly has an average negative radiative forcing of $-0.40 \pm 0.2 \text{ W m}^{-2}$ and cools the climate by increasing the Earth's albedo [11].

OCS is known to be one of the major long term contributors to the SSA. Large volcanic eruptions are another contributor to the

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SSA by direct injection of SO₂ into the stratosphere, but their effects are temporary [12]. It is difficult to assess the OCS contribution to SSA because of the large uncertainty in its sources and sinks [7,13,14]. For example, Watts estimates OCS global sources and sinks of 1.31 ± 0.25 and 1.66 ± 0.79 , respectively [13].

Trace gas isotopologues can give additional information about the atmospheric chemistry and dynamics [15,16]. Isotopes have been used to determine the contribution of OCS to SSA. Castleman et al. [17] found a $\delta_{\text{sulfate}} \sim 2.6\%$ for ³⁴S for the background SSA and concluded that tropical upwelling of OCS is a major contributor [17].

Chin and Davis [7] used a one dimensional photochemical model and, based on an OCS stratospheric lifetime of 10 years, concluded that the production rate of SSA from OCS oxidation is 2 to 5 times less than the amount of sulfur required to maintain the SSA. In contrast, Barkley et al. [10] found a more realistic stratospheric OCS lifetime of 64 ± 21 years using the measurements obtained by Atmospheric Chemistry Experiment (ACE) satellite corresponding to a stratospheric sink of $63\text{--}124 \text{ Gg yr}^{-1}$ ($34\text{--}66 \text{ GgS yr}^{-1}$) which is in the range of sulfur mass estimated by Chin and Davis [7] that is needed to sustain the SSA. Subsequently, Krysztofiak et al. [18] found a stratospheric OCS sink of $54 \pm 14 \text{ GgS yr}^{-1}$ using SPIRALE and SWIR balloon borne measurements in agreement with the conclusion of Barkley et al. [10].

Leung et al. [19] tried a different approach to estimate the contribution of OCS to the SSA by measuring the OCS isotopic fractionation. Leung et al. [19] found a fractionation factor of the $\epsilon \sim 73 \pm 8.6 \%$ for OC³⁴S with the MkIV balloon-borne FTS, implying that the SSA should be enriched in ³⁴S. Leung et al. [19] cited the study of Miller and Yung [20] that suggested a faster photolysis of OC³⁴S compared to OC³²S. Collusi et al. [21] also measured the absorption cross sections of OC³²S and OC³⁴S and concluded that the OC³⁴S absorption cross section is larger than that of OC³²S between $200 < \lambda(\text{nm}) < 260$ at 298 K near the absorption maximum.

Later, Hattori et al. [22] reported on extensive measurements of UV absorption cross sections of OCS isotopologues between 190 to 260 nm that are inconsistent with the results of Collusi et al. [21]. They found similar absorption cross section for OC³²S and OC³⁴S and estimated a small fractionation factor of $^{34}\epsilon \sim 1.1 \pm 4.2\%$. Lin et al. [23] reported on laboratory experiments on the photolysis of OCS. They found the fractionation factor $^{34}\epsilon$ to be between -10.5 to 5.3% .

In another study, Hattori et al. [24] analyzed the sulfur isotopic compositions of OCS using gas chromatography and mass spectrometry (GC-IRMS) of air collected at Kawasaki, Japan and reported a tropospheric value of $\delta^{34}\text{S}_0$ of $4.9 \pm 0.3\%$. Hattori et al. [24] used a similar analysis to Leung et al. [19] and estimated the stratospheric ³⁴S enrichment value to be -3.4 to 2.7% which is in agreement with the SSA enrichment value measured by Castleman et al. [17]. Hattori et al. [24] concluded that OCS is an important source of SSA.

Despite widespread tropospheric OCS observations [3,4], stratospheric OCS observations are more limited (e.g., [25–27]). More studies with wider geographical coverage will help determine the contribution of OCS to the SSA.

In this study we use ACE-FTS data to study OCS, O³⁴CS and the OC¹³S isotopologues in the stratosphere. Similar data from the balloon-borne MkIV FTS are also used. The main objectives are to investigate the global zonal and seasonal distributions of OCS, O¹³CS and OC³⁴S; and to study the isotopic composition of OCS in the stratospheric to assess its contribution to background SSA.

2. ACE satellite data

SCISAT, also known as the Atmospheric Chemistry Experiment (ACE), is a satellite developed by the Canadian Space Agency (CSA)

for infrared remote sensing of the Earth's atmospheric composition [28,29]. It was launched by NASA into a circular orbit at 650 km altitude with a high 74° inclination to the equator in August 2003. Routine measurements began in late February 2004. The main instrument on board SCISAT is a high resolution Fourier transform spectrometer (ACE-FTS). ACE-FTS has a spectral resolution of 0.02 cm^{-1} covering the spectral range of 750 to 4400 cm^{-1} (2.2 to $13.3 \mu\text{m}$). ACE-FTS uses the solar occultation technique which records atmospheric transmission spectra during sunrise and sunset in the limb geometry using the Sun as an infrared source.

Profiles of 35 trace gases, as well as 20 isotopologues are retrieved from ACE-FTS spectra using version 3.5/3.6 of the ACE-FTS data processing [30] with a vertical resolution of about 3 km [28]. ACE-FTS retrieves ¹⁶O¹²C³²S, ¹⁶O¹²C³⁴S and ¹⁶O¹³C³²S isotopologues of carbonyl sulfide, which have natural abundances of about 95%, 4% and 1% [31]. The pressure and temperature profiles as a function of altitude are first determined using selected CO₂ lines. Temperature profiles are determined by the relative intensity of selected CO₂ lines and the pressure profiles from the optical depth of the lines. Altitude registration is performed using information from the Canadian weather service model and the error in the final retrieved tangent height is about 50 m.

The OCS VMRs are retrieved in a second step, holding the temperature and pressure constant. To speed up processing, a set of microwindows (less than 0.5 cm^{-1} wide) is chosen for the retrieval. For each molecule these microwindows are chosen to minimize the interference with other molecules. The microwindow sets for the retrieval of OC³²S, OC³⁴S and O¹³CS are presented in tables S1–S3, respectively. The VMRs are adjusted by comparing the observed spectrum and the calculated spectrum from the forward model and minimizing the residuals. The atmospheric model consists of 150 spherical layers, each 1 km thick. A ray tracing program is used to determine the path for each tangent height and the Beer-Lambert law is used to calculate the spectrum. In this study version 3.5/3.6 of the ACE-FTS processing is used with most of the spectroscopic constants taken from the HITRAN 2004 database. The constants for OCS however were taken from an update that appeared in the HITRAN 2008 database [31].

3. Data analysis

More than 60,000 occultations are available for the 2004–2017 period in version 3.5/3.6 of ACE data. The ACE OCS data set contains profiles with unphysical spikes or oscillations, which need to be removed for optimal use of the results. These artifacts are due to missing data and low signal-to-noise ratio particularly for the minor isotopologues [30]. In the troposphere, clouds and aerosols also cause problems with the retrievals. The statistical retrieval error for the main OCS isotopologue is less than 2% up to 19 km and increases to $\sim 4\%$ at higher altitudes. The statistical error for OC³⁴S varies from 9 to 12% up to 17 km and increases to 15 to 50% at higher altitudes. The statistical error for O¹³CS is $\sim 20\text{--}33\%$ from 7–18 km and increases to 45–100% at higher altitudes. Several steps were taken to filter these bad data and improve the data quality. In the first step, negative VMR values were removed; while negative concentrations are allowed in ACE retrievals, they are not valid when calculating delta values. Secondly, the OCS VMRs with an uncertainty greater than 73 ppt were discarded. Also the VMRs for all isotopologues that are not determined within their uncertainty were discarded. In addition, the median absolute deviation (MAD) was calculated at each altitude to filter outliers. MAD is defined as $\text{MAD} = \text{median}_i(|x_i - \text{median}_j(x_j)|)$ and is less sensitive than the standard deviation to extreme outliers. Values with an absolute deviation greater than $3 \times \text{MAD}$ were discarded.

The ACE-FTS OCS retrieval also suffers from systematic errors that we estimate by comparison with an independent measure-

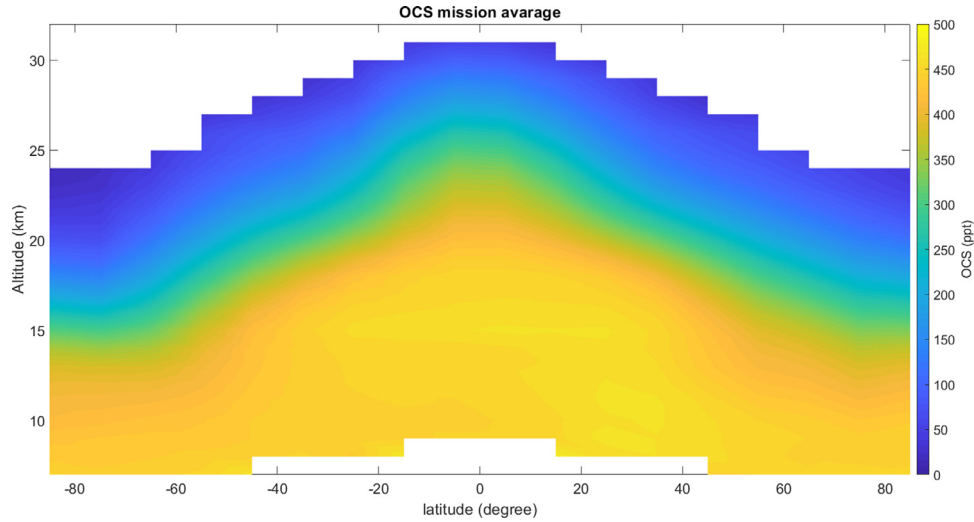


Fig. 1. Global atmospheric distribution of OCS from the ACE mission average. The OCS VMR values have been grouped together in 10° latitude bins.

ment made with the MkIV instrument at Ft. Sumner, New Mexico (35° N) and Esrange, Sweden and Fairbanks, Alaska (65° N). We found a percentage difference of 0.3–1% for 35° N and 0.16–4% for 65° N between the two independent measurements.

After filtering nonphysical data and outliers, the delta values and the corresponding fractionation uncertainties for each isotopologue were calculated,

$$\delta^{13}\text{C} = \left(\frac{^{13}\text{R}_{\text{sample}}}{^{13}\text{R}_{\text{std}}} - 1 \right) \times 1000\% \quad ^{13}\text{R} = \frac{[\text{O}^{13}\text{CS}]}{\text{OCS}} \quad (4)$$

$$\delta^{34}\text{S} = \left(\frac{^{34}\text{R}_{\text{sample}}}{^{34}\text{R}_{\text{std}}} - 1 \right) \times 1000\% \quad ^{34}\text{R} = \frac{[\text{OC}^{34}\text{S}]}{\text{OCS}} \quad (5)$$

in which the $^{13}\text{R}_{\text{std}} = 0.041583$ and $^{34}\text{R}_{\text{std}} = 0.010531$ values are from HITRAN 2016 database [31]. Finally, the $\delta^{34}\text{S}$ values with fractionation uncertainties larger than 800‰ and $\delta^{13}\text{C}$ values with uncertainties larger than 1000‰ were discarded.

4. Results and discussion

4.1. OCS global distribution

The global distribution of OCS using ACE-FTS data was studied by Barkley et al. [10]. They found an enhanced OCS concentration at 10–15 km between 0° and 30° N attributed to tropical biomass burning [4]. Barkley et al.'s results did not support previous model studies that suggested a large oceanic source at high SH latitudes [2]. In this study, we used ACE-FTS data to obtain a global distribution of OCS from the mission average. The ACE-FTS mission average VMRs from 2004 to 2017 are binned in 10° latitude bins on a 1 km altitude grid. Fig. 1 shows the OCS mission average global distribution from 2004 to 2017. A high OCS abundance is seen in the upper troposphere (UT) and lower stratosphere characteristic of upwelling in the tropics. This high OCS abundance over the tropics extends up to 20–25 km and decreases with increasing altitude and latitude. An enhancement of OCS is also observed in the NH between 0°–30° N up to 15 km, in agreement with Barkley et al. [10].

4.2. OCS vertical profile

The ACE-FTS OCS observations were sorted into 6 latitude bins covering the equator and mid-latitudes in the Northern Hemisphere (NH) and southern Hemisphere (SH). Fig. 2 shows the vertical profiles of ACE mission average OCS VMRs binned for 6 differ-

ent latitude bins 85° S–60° S, 60° S–30° S, 30° S–0° S, 0°–30° N, 30° N–60° N and 60° N–85° N on a 1 km altitude grid. As the altitude increases, OCS VMRs decrease as a result of photolysis and chemical reactions. The OCS VMRs remain constant within error over the tropics up to 15 km.

The NH and SH OCS VMRs were compared by computing tropospheric and stratospheric average values for the 6 latitude bins for the corresponding latitude bins in the NH and SH. Overall OCS tropospheric VMRs are about 10 ppt greater in the NH than SH for all latitude bins. In the stratosphere, in the mid-latitude and in the poles these differences are ~10 ppt and ~40 ppt. In addition, the ACE OCS altitude profiles were compared to the MkIV OCS measurements at 35° N and 65° N latitude. Data points from MkIV OCS measurements with the errors larger than 73×10^{-12} (73 ppt) were also discarded. This reduced the total number of data points from 756 to 572. Velazco et al. [32] performed a ACE-MkIV OCS comparison that used potential temperatures and equivalent latitudes from analyzed meteorological fields to find comparable ACE and MkIV profiles, despite the lack of spatio-temporal coincidence. This study found reasonable agreement, but with MkIV OCS somewhat larger.

4.3. OC^{34}S isotopologue global fractionation

The global distributions of OCS isotopologues provide information on the role of OCS in climate change [33]. As outlined in the introduction, there are contradictory views on the contribution of OCS to the background SSA. ACE-FTS data are used to obtain seasonal and zonal distributions of OC^{34}S fractionation. The $\delta^{34}\text{S}$ values were binned in 10° latitude bins and the global distribution of $\delta^{34}\text{S}$ during winter (DJF), spring (MAM), summer (JJA) and fall (SON) are presented in Fig. 3. Overall Fig. 3 shows an almost constant enrichment of OC^{34}S in the troposphere. As OC^{34}S penetrates into the stratosphere, there is a small fractionation of OC^{34}S that varies by season.

4.4. $\delta^{34}\text{S}$ altitude profile

The altitude profile of OC^{34}S fractionation obtained from ACE-FTS mission average between 2004 to 2017 for the latitude bins of 85° S–60° S, 60° S–30° S, 30° S–0° S, 0°–30° N, 30° N–60° N and 60° N–85° N were investigated. Fig. 4 shows that despite some fluctuations in the $\delta^{34}\text{S}$ values with altitude, these changes in ^{34}S enrichment are insignificant and lie within the error bars; therefore no

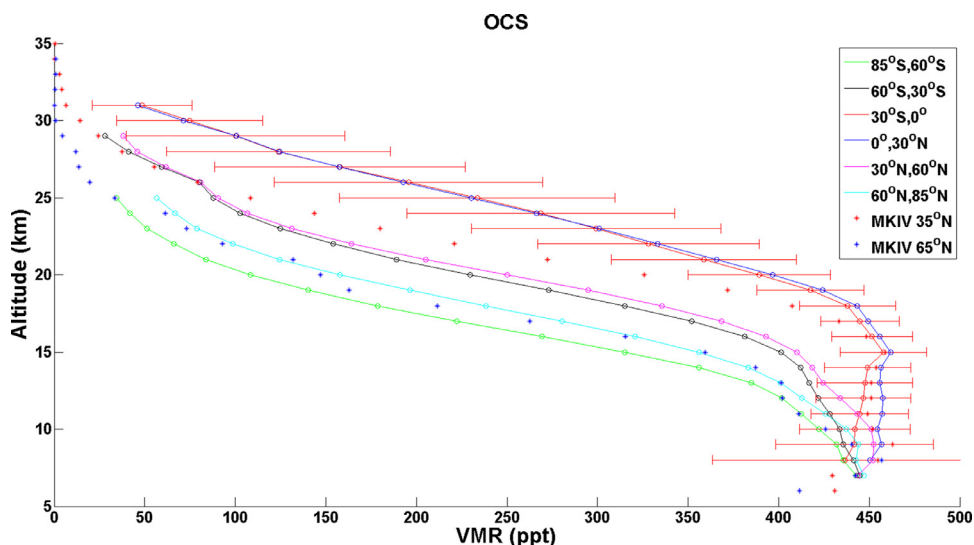


Fig. 2. Mean latitudinal OCS profiles measured by ACE on a 1 km vertical grid and averaged from February 2004 to December 2017 for the 6 latitude bins for 85° S–60° S, 60° S–30° S, 30° S–0° S, 0° –30° N, 30° N–60° N and 60° N–85° N, compared to the MkIV OCS measurements in the 35° N (red asterisks) and 65° N (blue asterisks). Because of similar error bars for all latitude bins, only error bars for one latitude bins are presented.

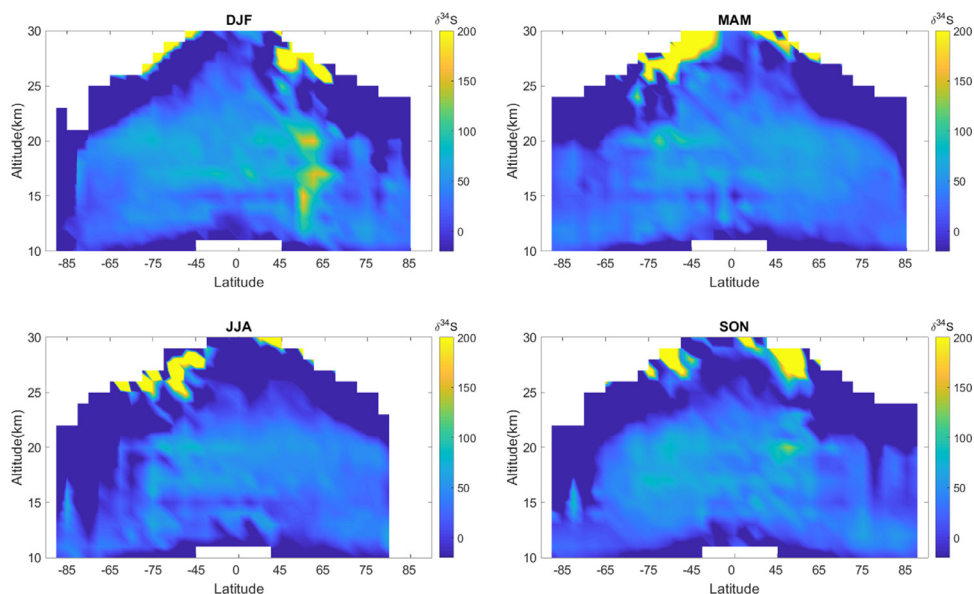


Fig. 3. Seasonal zonal distributions of $\delta^{34}\text{S}$ observed by ACE from 2004 to 2017. The $\delta^{34}\text{S}$ values have been grouped together in 10° latitude bins.

major enrichment of ^{34}S is observed for all latitude bins. The sharp increase in the OC^{34}S enrichment above 25 km, particularly in the tropics, is an artifact, related to the larger measurement errors.

4.5. O^{13}CS isotopologue global fractionation

The $\delta^{13}\text{C}$ values were binned in 10° latitude bins on a 1 km altitude grid with the data sorted into DJF, MAM, JJA and SON. The global distribution of $\delta^{13}\text{C}$ is presented in Fig. 5. An increasing enrichment in ^{13}C with altitude is observed in the stratosphere. Again a very sharp increase at the top of the altitude range may be an artifact.

As the stratospheric air increases in altitude, it becomes older and has been exposed to more UV light. The O^{13}CS enrichment with altitude results from the different absorption cross sections for O^{13}CS and OCS . O^{13}CS cross sections from 190 to 260 nm are less than the main OCS cross sections [22,34] and therefore O^{13}CS is photolyzed less. This causes the increase in $\delta^{13}\text{C}$ with increasing altitude as O^{12}CS is more fractionated by photolysis. The seasonal

variation of $\delta^{13}\text{C}$ (Fig. 5 (a–d)) shows more enrichment of O^{13}CS during DJF in the SH (Fig. 5 (a)) and during JJA in the NH (Fig. 5 (c)) at mid-latitudes due to the increased sunlight that leads to the more fractionation of OCS while the cold polar air in the NH (DJF) and in the SH (JJA) that is older and more enriched in O^{13}CS descends to the lower stratosphere (Fig. 5 (a & c)). We observe the formation of the Arctic and Antarctic polar vortices during DJF in the NH (Fig. 5 (a)) and during JJA in the SH (Fig. 5 (c)) that contain older air enriched in O^{13}CS . During MAM the enrichment begins to increase in the NH (Fig. 5 (b)) and during the SON, the enrichment begins to increase in the SH (Fig. 5 (d)).

4.6. $\delta^{13}\text{C}$ altitude profile

As for to OC^{34}S , the altitude profile of the average O^{13}CS enrichment was sorted into 6 different latitude bins covering the poles, mid-latitudes and tropics. Fig. 6 shows the change of the average $\delta^{13}\text{C}$ values as a function of altitude in the troposphere and strato-

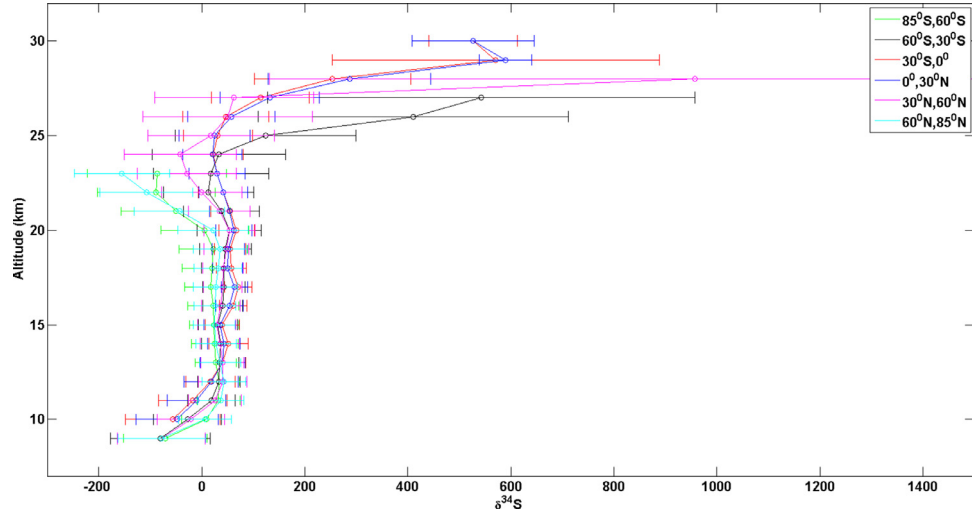


Fig. 4. Latitudinal $\delta^{34}\text{S}$ profiles measured by ACE on a 1 km vertical grid and averaged from February 2004 to December 2017. Latitudinal $\delta^{34}\text{S}$ profiles have been plotted for 6 bins for 85° S-60° S, 60° S-30° S, 30° S-0° S, 0° -30° N, 30° N-60° N and 60° N-85° N.

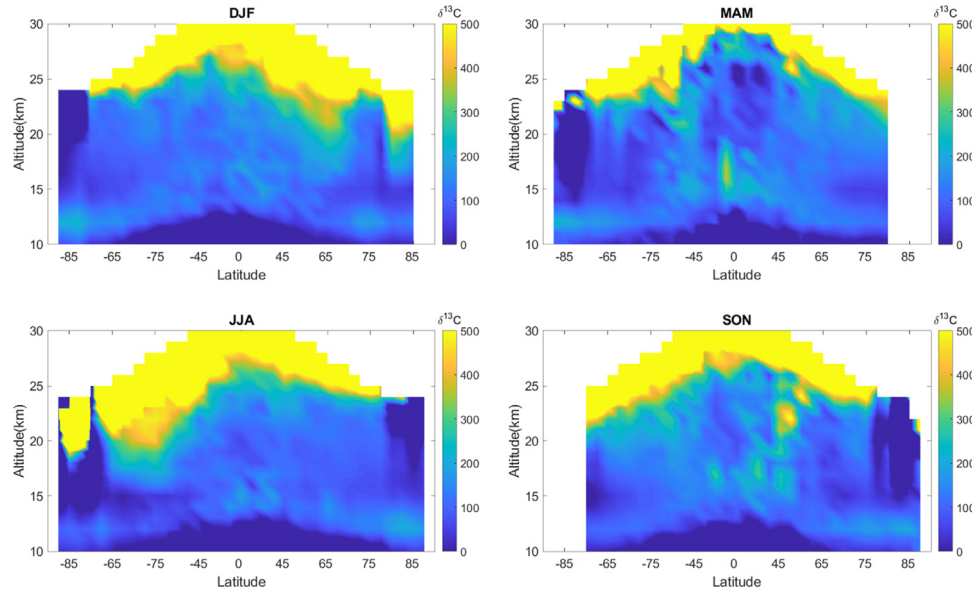


Fig. 5. Seasonal zonal distribution of $\delta^{13}\text{C}$ observed by ACE from 2004 to 2017. The enrichment values have been grouped together in 10° latitude bins.

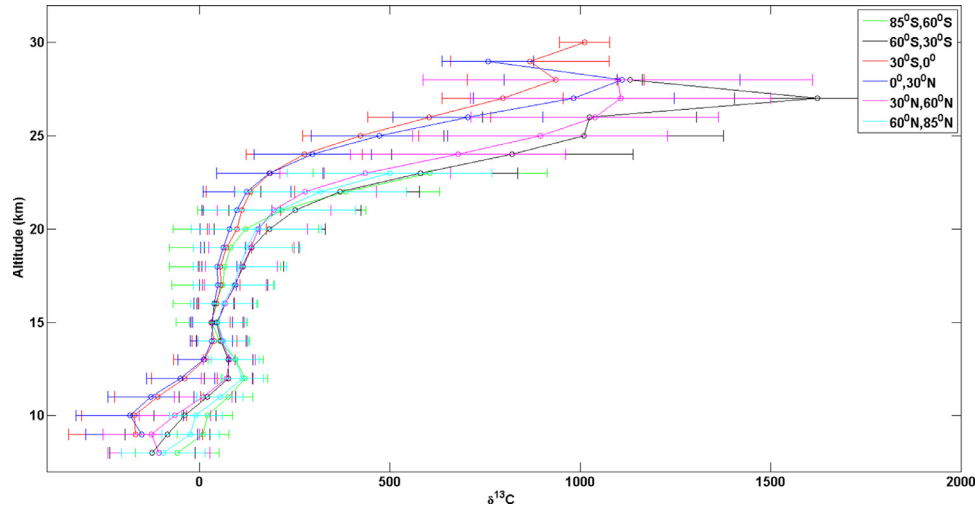


Fig. 6. Latitudinal $\delta^{13}\text{C}$ profiles measured by ACE on a 1 km vertical grid and averaged from February 2004 to December 2017. Latitudinal $\delta^{13}\text{C}$ profiles have been plotted for 6 latitude bins for 85° S-60° S, 60° S-30° S, 30° S-0° S, 0° -30° N, 30° N-60° N and 60° N-85° N.

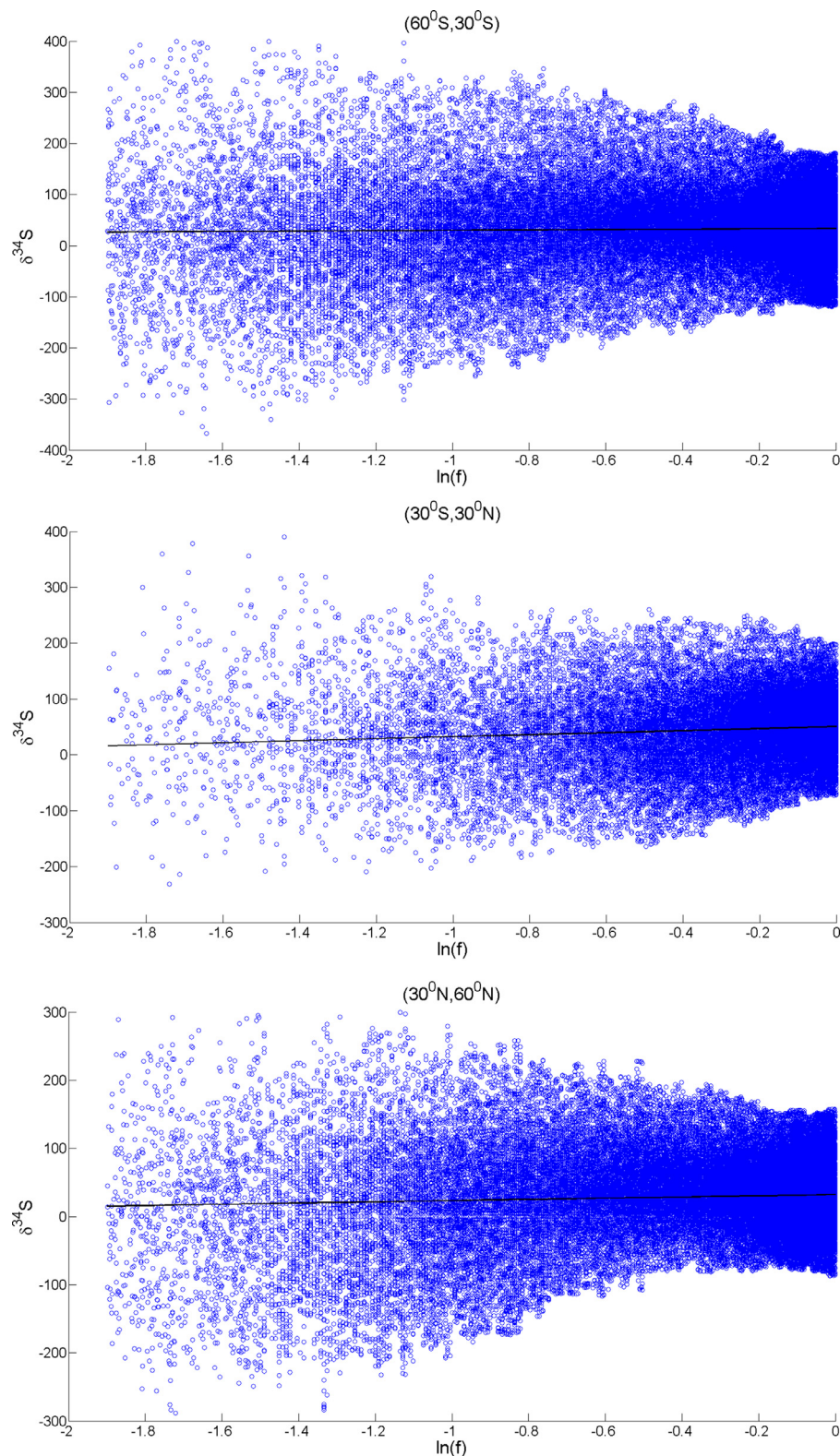
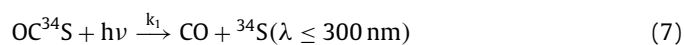
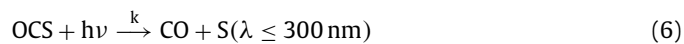


Fig. 7. ^{34}S abundance for stratospheric OCS as function of the unreacted fraction grouped in 3 latitude bins of 60°S – 30°S , 30°S – 30°N , 30°N – 60°N .

sphere. The enrichment of O^{13}CS increases with increasing altitude for all latitude bins.

4.7. Rayleigh distillation and isotopologue fractionation

The photolysis rate for different OCS isotopologues differs due to different cross sections in the 190–260 nm region which leads to the fractionation of OCS isotopologues,



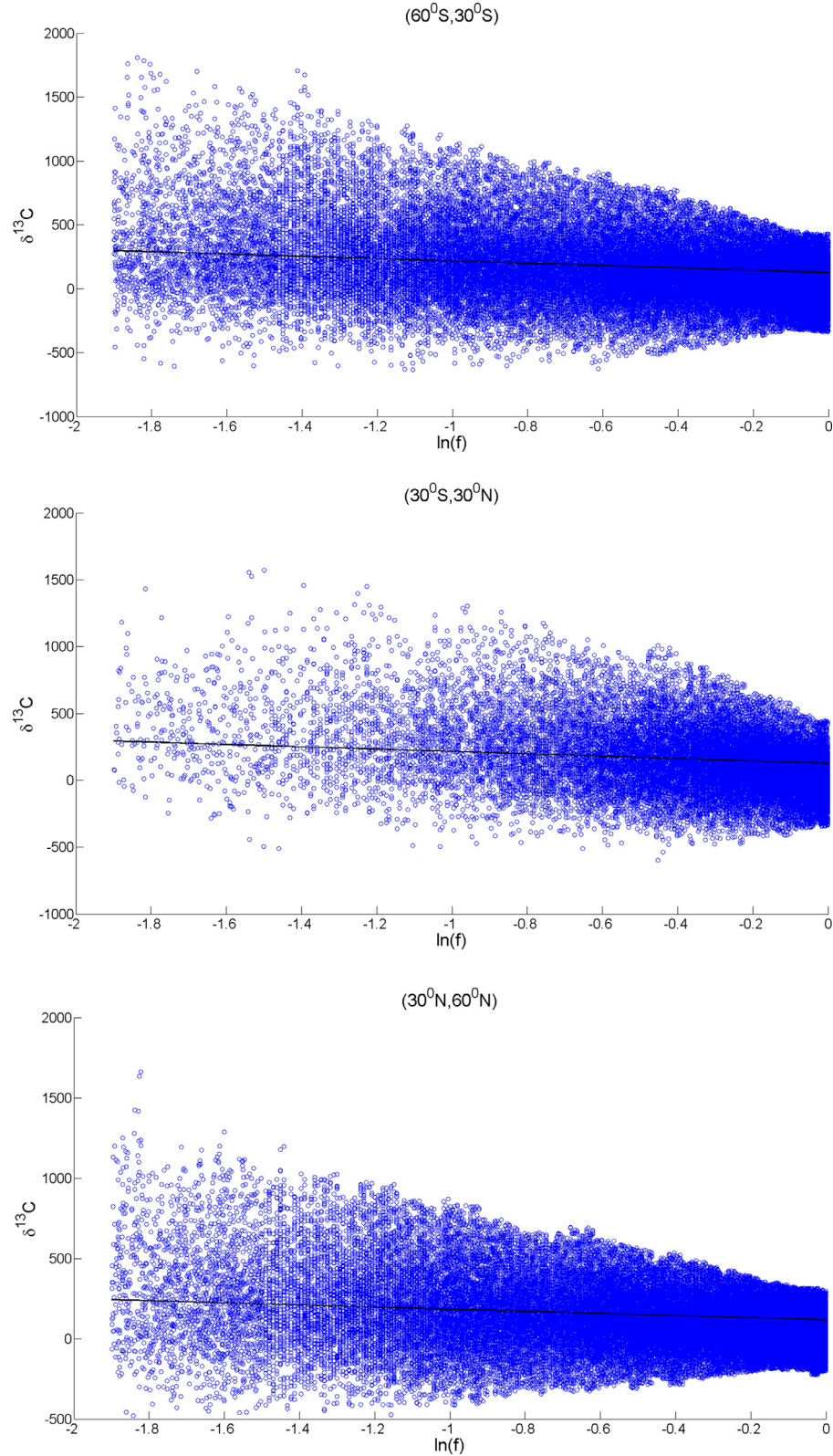


Fig. 8. ^{13}C abundance in stratospheric OCS as function of the unreacted fraction grouped in 3 latitude bins of 60°S – 30°S , 30°S – 30°N , 30°N – 60°N .

If the rate constants for reactions (1), (2) and (3) are independent of altitude, one can apply a Rayleigh distillation model in which the isotopic ratio at any given altitude z is related to the tropospheric isotopic ratio by Leung et al. [19],

$$R_z = R_0 f^{\alpha-1} \quad (9)$$

where $R_z = [\text{O}^{13}\text{C}^{18}\text{O}/\text{OCS}]_z$ ($x = 13, y = 34$) is the isotopic ratio for a given altitude, R_{trop} is the tropospheric isotopic ratio, $f = [\text{OCS}]_z / [\text{OCS}]_{\text{trop}}$ is the non-fractionated OCS for a given altitude z and $\alpha_i = k_i/k$ ($i=1,2$) is the photolysis rate ratio for the two isotopologues. To a good approximation, Eq. (9) leads to the expression,

$$\delta_z = \delta_0 + \epsilon \ln(f) \quad (10)$$

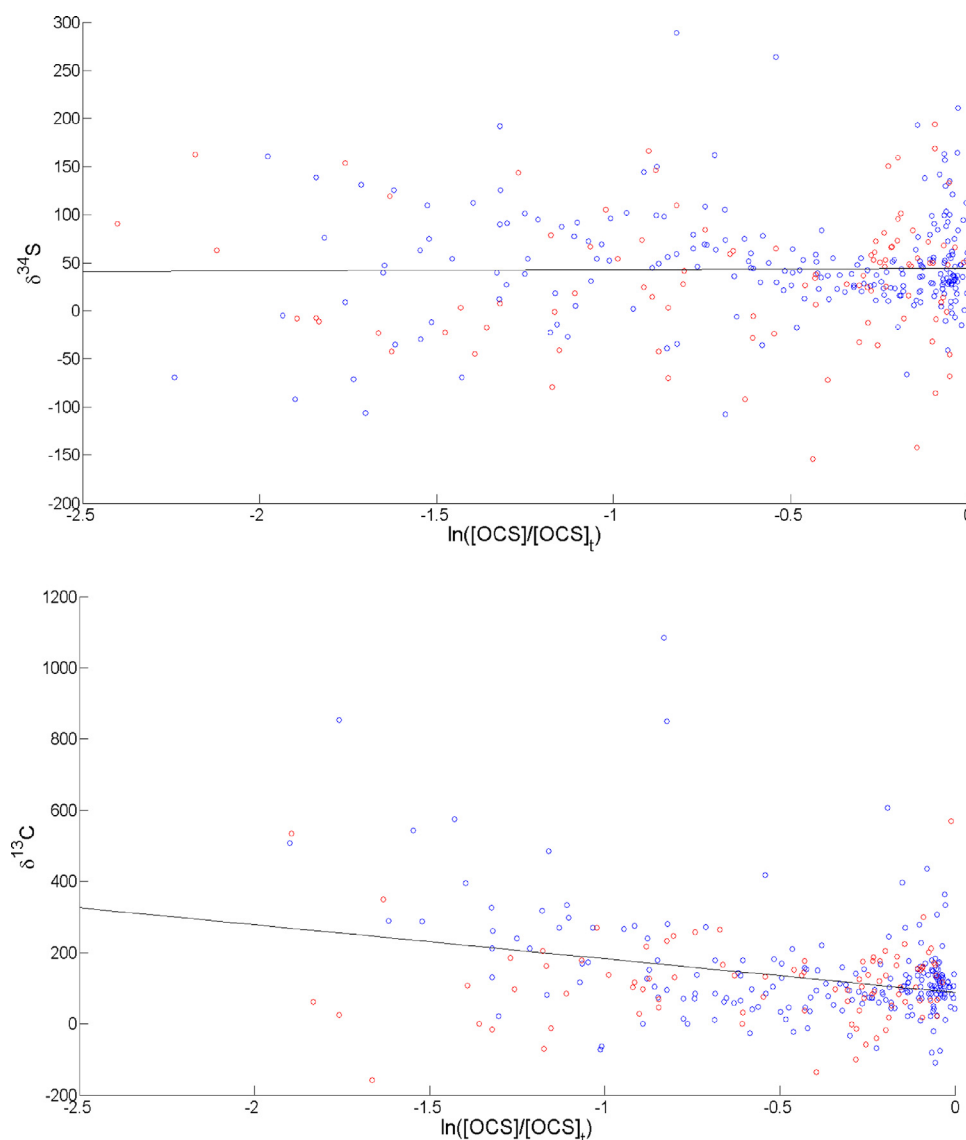


Fig. 9. OC³⁴S fractionation versus ln(*f*) (top) and O¹³CS fractionation versus ln(*f*) (bottom) plotted using MkIV data, obtained in the 35° N (blue) and 65° N (red).

where δ_z is the enrichment of the isotopologue of interest at a given altitude *z*, δ_0 is the tropospheric enrichment at the tropopause and $\epsilon = 1000 \times (\alpha - 1)$ is the enrichment factor of the isotopologue of interest in per mil.

4.7.1. Rayleigh distillation of OC³⁴S

We applied the Rayleigh distillation model to the ACE data for OC³⁴S isotopologue fractionation in the stratosphere. The $\delta^{34}\text{S}$ values were calculated for each individual ACE measurement and are plotted against ln(*f*). Non-physical data and outliers were discarded using the method described in Section 2. Tropospheric OCS VMRs ([OCS]_{trop}) required to calculate the *f* values are obtained by averaging the ACE-FTS OCS abundances in the troposphere. These values for the 3 latitude bins 60° S–30° S, 30° S–30° N and 30° N–60° N are 435 ppt, 443 ppt and 448 ppt, respectively. Fig. 7 (a–c) shows the Rayleigh plot of $\delta^{34}\text{S}$ for the 3 latitude bins. The linear trend of $\delta^{34}\text{S}$ values shows that the Rayleigh model is applicable for the OC³⁴S isotopologue [19]. The fractionation ($^{34}\epsilon$) can be determined from the slope of Rayleigh plots. A linear fit gives the $^{34}\epsilon$ values of 3.64 ± 0.57 , 5.91 ± 0.63 and $8.91 \pm 0.47\%$ for the latitude bins of 60° S–30° S, 30° S–30° N and 30° N–60° N, respectively. These frac-

tionation factors generally agree with the previous values of -1.9 to 1.6% calculated by Schmidt et al. [34] based on the theoretical calculation of OCS photolysis, the $1.1 \pm 4.2\%$ at 20 km from Hattori et al. [22] obtained from cross section measurements of OCS photolysis. The $^{34}\epsilon$ value for reaction (1) with OH is calculated to be -2.6% [9] and -14.8% (or -21.6% using measured rate constants) for reaction (2) with O atoms [35]. Including these values, Schmidt et al. [36] estimate total $^{34}\epsilon$ values of -5 to 0% in the stratosphere. Considering the systematic errors in our $^{34}\epsilon$ values from assuming a Rayleigh distillation model, it is not possible to separate the different sink mechanisms in the stratosphere.

The linear regression of ACE-FTS data for the fractionation of ^{34}S isotopologue for the 3 latitude bins in the tropics and mid-latitudes, also gives the $\delta_0^{34}\text{S}$ values 33.60 ± 0.57 , 44.92 ± 0.63 and $32.23 \pm 0.47\%$ respectively, at the tropopause, where OCS begins to fractionate.

The Rayleigh model of ^{34}S isotopologue shows a small fractionation for the equatorial and mid-latitude bins (Fig. 8). Considering the error bars, the estimated stratospheric ^{34}S fractionation from ACE-FTS in the tropics and mid-latitudes agrees with the observation of Castleman et al. [17] for SSA and Hattori et al. [22,24]. Our

study, as the first global observation of stratospheric OC³⁴S enrichment, concludes that OCS is a major contributor to the background SSA.

4.7.2. Rayleigh distillation of O¹³CS

Similar to the analysis of OC³⁴S, we use the Rayleigh distillation model in order to obtain the fractionation factor ($^{13}\epsilon$) for the same latitude bins used in section 4.7.1. The $\delta^{13}\text{C}$ values for each individual ACE measurement were calculated and plotted against $\ln(f)$, after discarding the non-physical values and outliers. Fig. 8 (a,b and c) shows the Rayleigh distillation plots for $\delta^{13}\text{C}$ for the 60° S–30° S, 30° S–30° N and 30° N–60° N latitude bins. A linear regression of ^{13}C Rayleigh fractionation plot gives the fractionation factors $^{13}\epsilon$ of -90 ± 1.4 , -88 ± 1.92 and $-65 \pm 1.16\%$ for the aforementioned latitude bins, respectively. This also gives the $\delta_0^{13}\text{C}$ values of 127.13 ± 1.4 , 126.82 ± 1.92 and $118.52 \pm 1.16\%$ at the tropopause, for the 3 latitude bins, respectively. Note that the negative sign in the slopes shows the increase of $\delta^{13}\text{C}$ with $\ln(f)$. Overall, the Rayleigh distillation model for O¹³CS shows an increasing enrichment with altitude. This increasing enrichment of O¹³CS with altitude generally agrees with Hattori et al. [22] who estimate a $^{13}\epsilon$ value of $-26.8 \pm 4.3\%$ at 20 km for photolysis from the absorption spectra. Schmidt et al.'s stratospheric photolysis values based on ab initio calculations are -3 to -14% and -5 to -15% for all three removal reactions [36].

4.8. MkIV measurements of OC³⁴S and O¹³CS fractionation

OCS fractionation has also been measured by the JPL MkIV FTIR spectrometer which covers the 650 to 5650 cm⁻¹ range at 0.01 cm⁻¹ resolution (60 cm OPD). From 24 high-altitude balloon flights, the MkIV has observed solar occultations allowing the retrieval of profiles of many gases and isotopologues from the clouds tops (~ 7 km) up to the balloon-float altitude (~ 40 km). Pre-2001 MkIV measurements of ³⁴S fractionation profiles of OCS were reported by Leung et al. [19]. For the present work, nine more balloon flights were included. Additionally, all spectra, including the pre-2001 ones, were re-analyzed using the latest spectroscopic line lists of OCS and interfering gases, and the latest spectral fitting and retrieval software. Five OCS windows covering 860 to 4120 cm⁻¹ were fitted and averaged to determine OC³²S. One contiguous window covering 2039 to 2076 cm⁻¹, centered on the ν_3 asymmetric OCS stretch band, was fitted for OC³⁴S.

Fig. 9 shows data obtained from MkIV measurements of OCS, OC³⁴S and O¹³CS isotopologues. The top panel shows the $\delta^{34}\text{S}$ plotted versus $\ln(f)$ ($f = [\text{OCS}]_z / [475 \text{ ppt}]$). Data points with fractionation uncertainty of 800‰ in $\delta^{34}\text{S}$ were discarded, reducing the number of data points to 314. The MkIV data give fractionation factors of $^{34}\epsilon = 4.9 \pm 5.31\%$ and ^{34}S fractionation of $41.72 \pm 5.31\%$ at the tropopause. Overall ³⁴S fractionation obtained from MkIV data shows a good agreement with ACE-FTS data, within the error bars. (Fig. 7).

The bottom panel in Fig. 9 shows the O¹³CS fractionation. Data points with fractionation uncertainty larger than 1000‰ were discarded, reducing the number of data points to 295. The MkIV data shows a O¹³CS enrichment factor of $^{13}\epsilon = -95.3 \pm 12.7\%$ and $\delta_0^{13}\text{C}$ value of $87.6 \pm 12.68\%$ at the tropopause. The MkIV data also show an increasing enrichment for O¹³CS isotopologue, which is in agreement with ACE-FTS observation of O¹³CS (Fig. 8).

5. Summary and conclusions

We used ACE-FTS measurements of OCS, OC³⁴S and O¹³CS to study the zonal and seasonal profiles of stratospheric OCS. The ACE global distribution shows an uplift of OCS-rich air from the tropics into the stratosphere. In the stratosphere as OCS is destroyed it

moves poleward and then downward due to the Brewer–Dobson circulation.

The atmospheric fractionation of OCS isotopologues was studied. ACE and MkIV data show an almost constant relative abundance of OC³⁴S with a small fractionation in the stratosphere. This confirms that OCS is a major contributor to the background SSA because the observed OCS fractionation is similar to that measured in SSA. ACE and MkIV data also show an increasing enrichment of O¹³CS with increasing altitude consistent with absorption cross sections measured in the laboratory. MkIV measurements show a reasonable agreement with ACE data within error bars.

Data availability

The ACE-FTS freely available at <https://ace.uwaterloo.ca> after registration.

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Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jqsrt.2019.06.033.

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