Chapter 2: Isotopic fractionation of carbonyl sulfide in the atmosphere: Determination of the apparent isotopic enrichment factor of stratospheric processing of OCS*

2.1 Introduction

Carbonyl sulfide, OCS, is a substantial contributor to the background SSA. However, it has been difficult to ascertain the actual extent of its contribution from mass balance considerations alone, given the associated uncertainties of the budget for global OCS sources and sinks [*Chin and Davis*, 1995; *Watts*, 2000].

In addition, atmospheric models of stratospheric sulfate which have OCS as the only significant source of SSA sulfur under-predict the observed aerosol concentrations below ~20 km, but overestimate them at higher altitudes [*Hofmann*, 1991]. It is likely that additional sulfur sources may contribute significantly to SSA in the lower stratosphere. Recent studies have reported that inclusion of elevated SO_2 levels into the stratosphere due to injection by deep-convective events in the tropics at resulted in a better match to observed stratospheric sulfate aerosol profiles [*Kjellstrom*, 1998; *Weisenstein et al.*, 1997].

The identified pathways for OCS destruction in the gas phase are photodissociation, and to a lesser extent, oxidation by O and OH radicals [*Chin and Davis*, 1995]. Lacking further evidence, it is also possible that there exist alternative, still unknown processes for the stratospheric processing of OCS, although recent work has

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ruled out the possible importance of heterogeneous oxidation of OCS by H_2O_2 [*Dalleska et al.*, 2000]

In order to assess the contribution of carbonyl sulfide to stratospheric sulfate aerosol (SSA), we examined the $OC^{34}S$ and $OC^{32}S$ concentration profiles in the infrared limb-transmittance spectra acquired by the JPL MkIV instrument [*Toon*, 1991].

We use the vertical profile of both $OC^{34}S$ and $OC^{32}S$ isotopomers from the high resolution IR spectra previously used by Griffith et al. in their study of N_2O isotopomers [*Griffith et al.*, 2000], plus additional spectra recorded in the year 2000, to establish the sign and magnitude of sulfur isotope fractionation resulting from the stratospheric processing of OCS. Combining this information with previous data on the sulfur isotopic ratio in SSA particles, and with recent estimates of the tropospheric OCS isotopic composition, we are able to arrive at an upper limit for the contribution of OCS to the SSA.

2.2. Experimental Procedure

Isotopologues of OCS can be distinguished on the basis of their ro-vibrational band spectra in the near infrared region. Here, we analyze nine sets of high resolution infrared solar occultation spectra recorded by the MkIV instrument on balloon flights launched from Fort Summer, New Mexico (34N), Esrange, Sweden (68N), Fairbanks, Alaska (64N), Lynn Lake, Manitoba (57N), and Daggett, California (34N) between 1992 and 2000 [*Toon et al.*, 1999; *Toon*, 1991]. For each balloon flight, spectra were typically acquired at tangent altitudes between about 5 km and 40 km altitude, at 1 to 3 km intervals.

The spectral region between 2041 and 2077 cm^{-1}, centered on the ν_3 asymmetric OC^{32}S stretch at 2054 cm^{-1}, was analyzed using the GFIT program, which involves a least squares regression of known spectral library data to the acquired spectra. A sixty 1-km layer model of the atmosphere was used. Spectroscopic parameters from the HITRAN 1996 were supplemented by recent measurements of OCS [*Strugariu et al.*, 1998] and of isotopic O_3 absorption bands [*Barbe*, 2001].

The 50 cm^{-1} region centered on the weaker ν_1 OCS band at 850 cm^{-1} was also examined to test the robustness of the analysis, the results being in agreement with those from the 2041-2077 cm^{-1} region.

2.3. Results and Discussion

The sulfur isotopic fractionation ratio of the OC^{34}S isotopomer with respect to the OC^{32}S isotopomer, δ^{34}S, is defined as:

$$\delta^{34}S = 1000 \times \left[\frac{({}^{34}S/{}^{32}S)_{sample}}{({}^{34}S/{}^{32}S)_{s\tan dard}} - 1 \right] \tag{2.1}$$

The standard is meteoretic Cañon Diablo troilite. Because of the relatively large natural abundance of ^{34}S (4.2%) compared those of the heavier isotopes of carbon and oxygen, OC^{34}S and OC^{32}S are in essence the only relevant isotopologues. Therefore, the analysis of the spectra of OCS isotopologues is simpler than in the case of N_2O, which has 2 ^{15}N positional isotopomers, ^{15}N^{14}NO and ^{14}N^{15}NO, in addition to the parent ^{14}N^{14}NO isotopologue.

Isotope fractionation will result during the photolysis of OCS if the ratio of actinic light absorbances differed from the relative isotopomer concentrations [*Miller and Yung*, 2000]:

$$OC^{34}S + h\nu \xrightarrow{k_2} {}^{34}S + CO \tag{2.2}$$

$$OC^{32}S + h\nu \xrightarrow{k_3} {}^{32}S + CO \tag{2.3}$$

δ^{34}S is usually reported for local concentrations at a particular altitude, rather than for slant column abundances. However, to avoid the ambiguities associated with the retrieval of local concentrations from slant column abundances, we based our analysis on raw slant column abundances. Since slant column abundances are strongly weighted to the tangent altitudes, they give a good approximation to the conventionally defined δ^{34}S at that tangent altitude, especially for gases like OCS and N_2O whose volume mixing ratio decreases with altitude [*Griffith et al.*, 2000]. The volume mixing ratio (vmr) profile for OCS, plotted against tangent altitude, is shown in Figure 2.1.

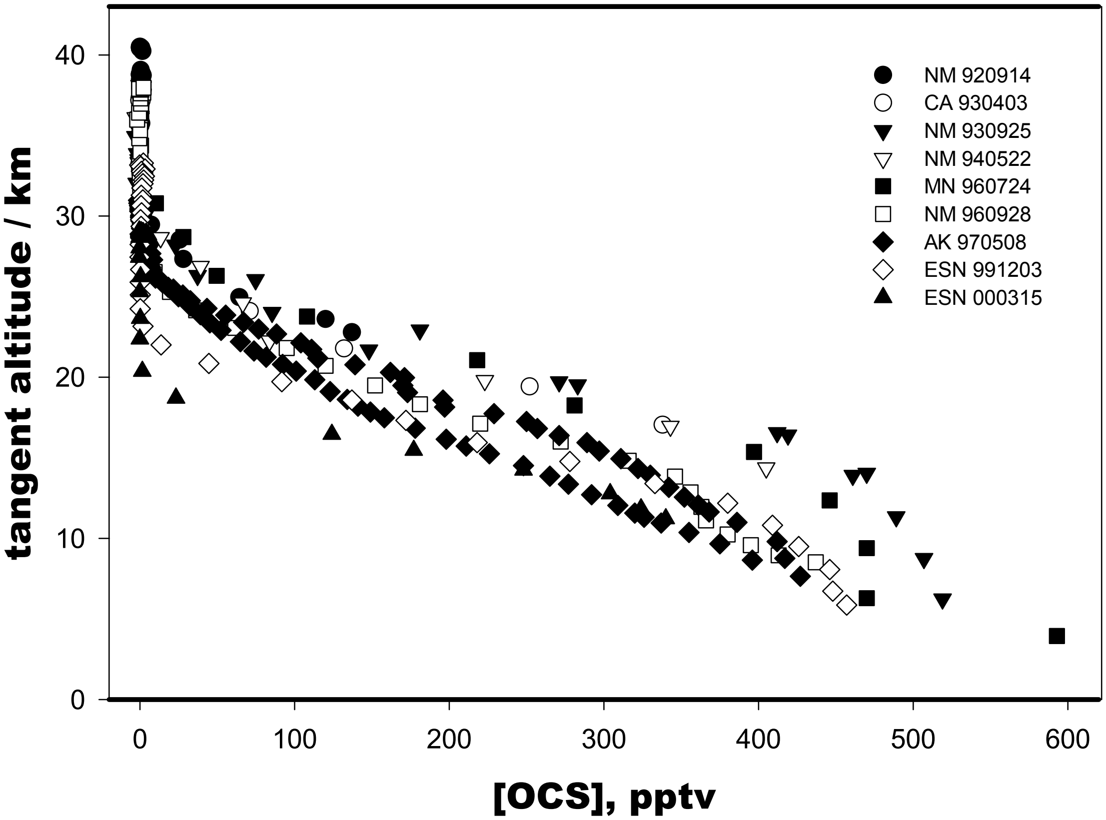

Figure 2.1. Tangent height vertical profiles for total OCS (i.e.: $OC^{34}S + OC^{32}S$) partial pressures The locations and launch dates of the missions are identified in the legend as: MN = Manitoba, Canada; ESN = Esrange, Sweden; ALK = Alaska, NM = New Mexico; and CA = California, USA, and YY/MM/DD time format, respectively. We have combined profiles that were measured during the same flight.

If the ratio k_2/k_3 were independent of altitude, the isotopic enrichment of OCS could be analyzed in terms of a Rayleigh distillation [*Griffith et al.*, 2000; *Rahn and Wahlen*, 1997]. For OCS at any altitude, the isotopic ratio R would be then related to the tropospheric isotopic value R_o by:

$$R = R_0 f^{\alpha - 1} \qquad (2.4)$$

where $f = [OCS]_{z/}[OCS]_{troposphere}$ is the fraction of unphotolyzed OCS, and α the ratio of photolysis rates for the heavier to the lighter isotopomer. This leads, as a good approximation, to

$$\delta = \delta_0 + \varepsilon \ln f \qquad (2.5)$$

where δ_0 is the value of δ at the tropopause and $\varepsilon = 1000 \times (\alpha-1)$ is the isotopic enrichment factor. Deviation from linearity would point to the involvement of additional losses, or to the dependence of mass transport parameters on altitude. Within the uncertainty in the data, the above analysis appears to be valid (Fig. 2.2).

The present analysis is very similar to that performed by Griffith et al, for N_2O. However, the natural abundance of OCS at the tropopause is ~0.5 ppbv, compared to 315 ppbv for N_2O. This explains at least in part the greater degree of scatter in the OCS Rayleigh plot compared to that for N_2O [*Griffith et al.*, 2000]. However, uncertainties reported by the spectral fitting algorithm (not reported) are even larger. These uncertainties arise from systematic errors due to inadequacies in the spectroscopic library, which are independent of altitude. However, systematic errors affect $OC^{32}S$ and $OC^{34}S$ measurements to similar extents and, therefore, should not modify the calculated sulfur isotopic enrichment factor, ε. However, as noted by Griffith et al. (2000), the measured ε's are sensitive to errors that are not independent of altitude and/or absorption strength in the spectra, such as zero offsets, temperature profiles and assumed line broadening coefficients.

We performed sensitivity analyses on these factors and found that the results are indeed robust. Calculated $\delta^{34}S$ values are unreliable below ~10 km because of the increasing atmospheric opacity, and above about 20 km, where the $OC^{34}S$ absorption lines become very weak in comparison with the spectral noise. These values were therefore excluded from the Rayleigh plot analysis (Fig. 2.2).

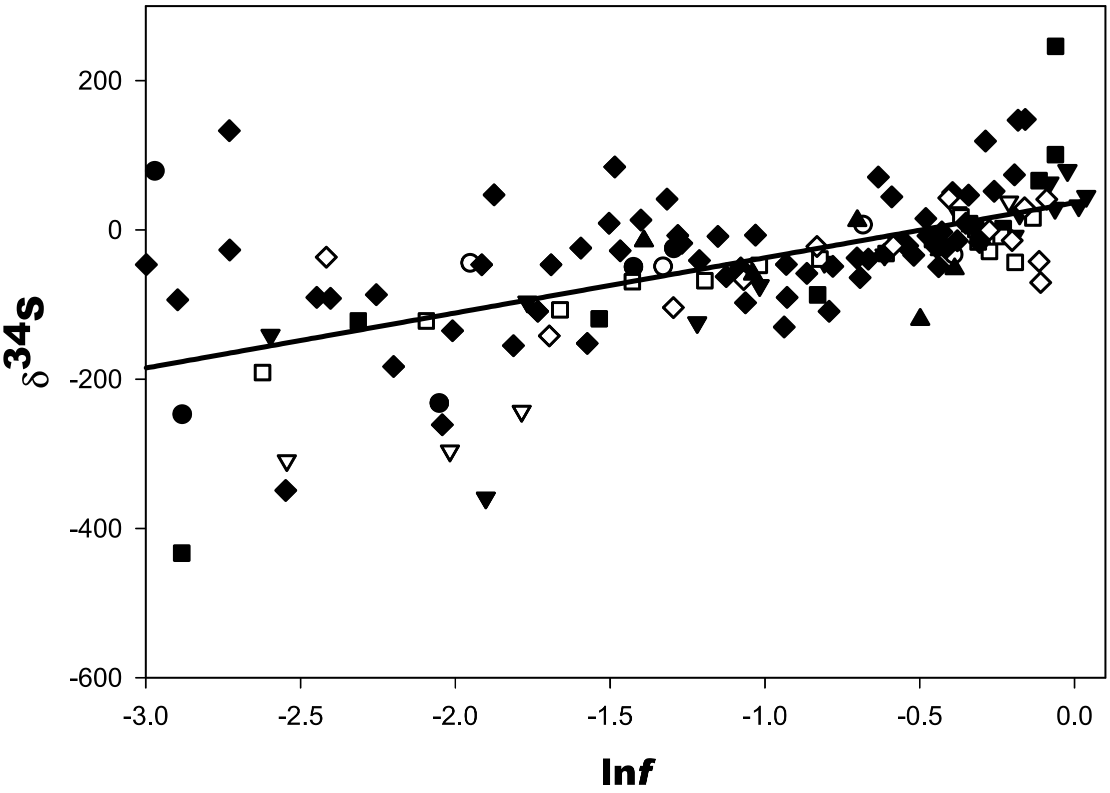

Figure 2.2. ^{34}S abundance in stratospheric OCS as function of the unreacted fraction. The mixing ratio of OCS in the troposphere was assumed to be 0.5. Flights are identified as in Figure 2.1.

Enrichment factors were calculated both using the entire dataset, which includes all flights, and using data from individual flights, provided they contained sufficient data to perform meaningful statistical analyses. Regression parameters were derived by assigning individual points, which were weighted proportional to 1/error^2 [*Bevington*, 1969]. The enrichment factor calculated by averaging the results from individual flights were also weighted as 1/(standard error)^2. The results are reported in Table 2.1. It is apparent that, despite the considerable variability between the values of individual missions, the enrichment factor calculated from the entire dataset is in good agreement with the weighted average of the ε's.

Table 2.1. Calculated Enrichment factors

Flight	**Enrichment Factor**	**Standard Error**
April 1993, CA	94.2	20.2
September 1996, NM	120.5	30
May 1997, AK	70.4	6.2
July 1997, ALK	59.1	13.6
December 1999, ESN	80.8	19
Weighted average of above	71.1	21.9
Average of all flights	73.8	8.6

The possible mechanisms of OCS destruction in the lower stratosphere include photolysis, which is believed to account for most of OCS processing, and oxidation by O or OH [*Chin and Davis*, 1995]. The relative importance of such processes varies with the concentrations of the oxidizing species and the opacity of the atmosphere, i.e., with altitude. If the actual sulfur isotopic enrichment factors associated with the different processes were to differ significantly, Rayleigh plots should deviate from linearity. At the same time, apparent enrichment factors may also vary with latitude and season. However, it is impossible to determine whether seasonal or latitudinal dependencies exist from the limited number of field missions. The Rayleigh plots generated from either the whole dataset or from individual missions do not show deviations from linearity within the level of uncertainty and, therefore, more accurate or more comprehensive data would be needed to expose such dependencies.

From the local ozone concentrations, which were also retrieved from the same spectral dataset, it is possible to test the hypothesis that photolysis by solar radiation that is screened by ozone is the major loss channel for OCS in the stratosphere. The actinic radiation at the lower altitudes peaks at about 215 nm, which lies about 10 nm below the absorption maximum of OCS at about 223 nm [*Wu et al.*, 1999]. Combining the actinic photon flux filtered by the ozone column from the top of the column down to altitude z:

$$I_z = I_\infty \exp\{-\chi_{O_3,215nm} \int_\infty^Z [O_3]_z \, dz\} \approx a - bz \qquad (2.6)$$

with the OCS mass balance:

$$k_t \{[OCS]_z - [OCS]_{z+dz}\} = I_z \chi_{OCS,215nm} [OCS]_z \, dz \qquad (2.7)$$

we obtain:

$$\ln \frac{[OCS]z}{[OCS]_{z\,\min}} = A[1 - \exp[\gamma(z - z_{\min})] \qquad (2.8)$$

where k_t [time^{-1}] is the rate constant for vertical ascent, the χ's [concentration^{-1} distance^{-1}] are the base-*e* extinction coefficients and A and γ are combinations of spectral and transport parameters. Equation 2.8 provides a realistic representation of the experimental [OCS] vs z data (Fig. 2.3). It is important to note that observations were made from a balloon flight flying at high latitudes and outside the polar vortex, but before it had dissipated. The [OCS] vertical profile is therefore not affected by latitudinal transport, the effects of which are not considered in the above analysis. This restriction does not

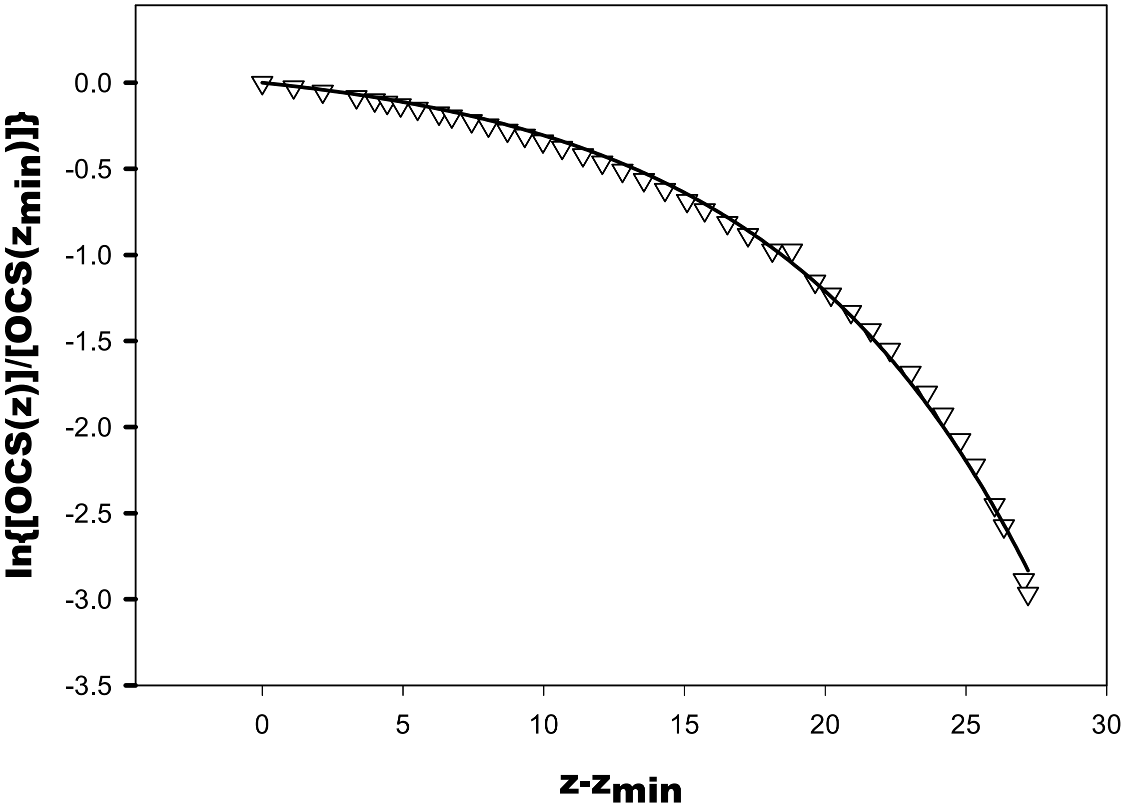

Figure 2.3: Normalized OCS concentration as a function of normalized altitude. z_{min} in this case is 7.6 km. The solid line is a regression of equation 9 to experimental data. The data used was from the mission launched from Fairbanks Alaska in May, 1997 (AK 970508).

detract from the conclusion that OCS photodissociation is the major stratospheric loss channel for OCS.

It is important to note that regardless of the origin of the isotopic fractionation, the observed enrichment factor is an apparent enrichment factor, and is estimated to be 30-50% lower than the actual isotopic enrichment factor due to the effects of eddy diffusion.

The observed enrichment factor has a large positive value, in contrast to the large negative value measured for stratospheric N_2O [*Griffith et al.*, 2000]. The contrasting behaviors arise from the fact that the actinic radiation in both cases is centered about 215 nm, which lies to the blue of the OCS absorption maximum at 223 nm, but to the red of that for N_2O at 183 nm. According to the recent analysis of the spectral shifts induced by isotope substitution [*Miller and Yung*, 2000], the photolysis of $OC^{34}S$, as well as the lighter, parent isotopomer of N_2O, should proceed at faster rates. Thus, the products of the photolysis of OCS should be enriched in ^{34}S, i.e., $\varepsilon > 0$, as observed. The theory, which is based on an equilibrium analysis of zero point energy effects, is qualitatively correct but could not actually predict ε values in the case of N_2O photolysis.

Zhang et al., [2000] suggested that these discrepancies might arise from the dissimilarly populated hot-bending bands of the various isotopologues/isotopomers, a phenomenon not addressed in the simple Miller and Yung model [*Zhang et al.*, 2000], which assumes that the potential energy surfaces are not affected by the mass of the nuclei. Furthermore, the upper state is assumed in the Miller and Yung model to be purely repulsive, so the possible effects of isotopic substitution on the energy levels of the upper state are not addressed. Recent calculations by *Johnson et al.* [2001] show that, at least for the case of N_2O photolysis, that the effect of isotopic substitution on the upper states is as, if not more, important, than the lowering of the ZPE. These issues are elaborated upon in Chapter 4.

2.4. Implications for the genesis of the stratospheric sulfate

As noted previously, atmospheric OCS fluxes are rather poorly constrained by existing measurements. Based on known chemical and photochemical rates, *Chin and Davis* [1995] estimated that less than 10% of the OCS transported into the stratosphere is actually destroyed there. The remainder re-enters the troposphere. Based on this appraisal, our enrichment factor of $\varepsilon \sim +73$ ‰, and *Krouse and Grinenko*'s [1991] estimate of $\delta^{34}S \sim 11$‰ for tropospheric OCS, we infer from mass balance considerations that any sulfate produced from OCS should have a $\delta^{34}S_{sulfate} \sim 80$ ‰. [From $\delta^{34}S_{sulfate}(1\text{-}f) + \delta^{34}S\, f = \delta_0{}^{34}S$, where $\delta^{34}S = 11$‰ + 73 ln (0.9) (Equation 2.5)]. In contrast, *Castleman et al*. [1974] found that in background SSA $\delta^{34}S_{sulfate} \sim 2.6$‰.

At first glance, this wide discrepancy seems to suggest that carbonyl sulfide can contribute negligibly to stratospheric aerosol during volcanically quiescent periods. In fact, *Leung et al.* [2002] assumed that the $\delta^{34}S$ values for atmospheric SO_2 and background aerosol were identical within 5‰, and estimated that OCS contributes less than 6% of the SSA sulfur budget.

However, the predicted $\delta^{34}S \sim 80$ ‰ value for the product sulfate depends on the assumed stratospheric conversion of OCS via Eq. 2.5. Thus, the $\delta^{34}S$ for the resultant sulfate decreases from ~84‰ at $f = 0$, to the tropospheric value for OCS, $\delta^{34}S \sim 11$‰ at 100 % conversion. In other words, as f increases, the discrepancy between predicted and observed $\delta^{34}S$'s for SSA converges to the difference between 2.6 and 11‰. Therefore, most of the discrepancy would be removed if *Chin and Davis* [1995] had underestimated the extent of OCS conversion. In that event, the discrepancy would ultimately be associated with the tentative estimates of $\delta^{34}S$ in tropospheric OCS made by *Krouse and Grinenko* [1991].

Moreover, this analysis assumes either that the oxidation of SO_2 to sulfate is isotopically indifferent, or that SO_2 to sulfate conversion is complete. As we will show in Chapter 4, there is in fact a large and positive isotopic fractionation ratio associated with the homogeneous oxidation of SO_2 by OH, and a smaller but nevertheless positive isotopic enrichment factor associated with heterogenous SO_2 processing.

These caveats underscore the need for more accurate sulfur isotopic data, which are experimentally accessible, to provide definitive clues regarding the origin of background stratospheric sulfate aerosols.

2.5. Conclusions

From the analysis of high-resolution infrared spectra of the terrestrial atmosphere obtained by balloon flights spanning ten years, which cover various latitudes and seasons, we reach the following conclusions:

i) The apparent ^{34}S enrichment factor for stratospheric processing of carbonyl sulfide is $\varepsilon = 73 \pm 8‰$.

ii) The vertical profile of OCS concentrations can be quantitatively accounted for by photolysis under solar radiation screened by the ozone layer

iii) A positive ε value is only qualitatively consistent with an equilibrium analysis of zero point energy effects on the UV absorption spectrum of OCS.

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References

Barbe, A., Personal Communcation, 2001.

Bevington, P.R., *Data Reduction and Error Analysis for the Physical Sciences*, 336 pp., McGraw-Hill,, 1969.

Chin, M., and D.D. Davis, A reanalysis of carbonyl sulfide as a source of stratospheric background sulfur aerosol, *J. Geophys. Res.*, *100*, 8993-9005, 1995.

Dalleska, N.F., A.J. Colussi, A.M. Hyldahl, and M.R. Hoffmann, Rates and mechanism of carbonyl sulfide oxidation by peroxides in concentrated sulfuric acid, *J. Phys. Chem. - A*, *104*, 10794-10796, 2000.

Griffith, D.W.T., G.C. Toon, B. Sen, J.F. Blavier, and R.A. Toth, Vertical profiles of nitrous oxide isotopomer fractionation measured in the stratosphere, *Geophys. Res. Lett.*, *27*, 2485-2488, 2000.

Hofmann, D.J., Aircraft sulphur emissions, *Nature*, *349*, 659, 1991.

Kjellstrom, E., A Three dimensional global model study of carbonyl sulfide in the troposphere and the lower stratosphere, *J. Atmos. Chem.*, *29*, 151-177, 1998.

Miller, C.E., and Y.L. Yung, Photo-induced isotopic fractionation, *J. Geophys. Res.*, *105*, 29039-29051, 2000.

Rahn, T., and M. Wahlen, Stable isotope enrichment in stratospheric nitrous oxide, *Science*, *278*, 1776-1778, 1997.

Strugariu, T., S. Naim, A. Fayt, H. Bredohl, J.F. Blavier, and I. Dubois, Fourier transformation spectrscopy of O-18-enriched carbonyl sulfide form 1825 to 2700 cm^{-1}, *J. Mol. Spec.*, *189*, 206-219, 1998.

Toon, G., J. Blavier, B. Sen, J. Margitan, C. Webster, R. May, D. Fahey, R. Gao, L. Del Negro, M. Proffitt, J. Elkins, P. Romashkin, D. Hurst, S. Oltmans, E. Atlas, S. Schauffler, F. Flocke, T. Bui, R. Stimpfle, G. Bonne, P. Voss, and R. Cohen, Comparison of MkIV balloon and ER-2 aircraft measurements of atmospheric trace gases, *J. Geophys. Res. - Atmopheres*, *104*, 26779-26790, 1999.

Toon, G.C., The JPL MkIV interferometer, *Optics and Photonics News*, 19-21, 1991.

Watts, S.F., The mass budgets of carbonyl sulfide, dimethyl sulfide, carbon disulfide and hydrogen sulfide, *Atmos. Environ.*, *34*, 761-779, 2000.

Weisenstein, D.K., G.K. Yue, M.K.W. Ko, N.-D. Sze, J.M. Rodriguez, and C.J. Scott, A two-dimensional model of sulfur species and aerosols, *J. Geophys. Res.*, *102*, 13019-13035, 1997.

Wu, C.Y.R., F.Z. Chen, and D.L. Judge, Temperature dependent photoabsorption cross sections of OCS in the 2000-2600 A region, *J. Quant. Spectrosc. Radiat. Transfer*, *61*, 265-71, 1999.

Zhang, H., P.O. Wennberg, V.H. Wu, and G.A. Blake, Fractionation of $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$ during photolysis at 213 nm, *Geophys. Res. Lett.*, *27*, 2481-2484, 2000.

Addendum

It has been suggested that data at high altitudes, where mixing ratios of OCS are very low, should be excluded from the analysis entirely. In a log/linear plot, the weight of the data at high altitudes would be disproportionately high. Furthermore, because the isotopic enrichment factor derived from the data is a composite of enrichment factors from all the OCS loss pathways, the overall enrichment factor may in fact change with altitude. We performed an analysis using only those data where $f > 0.05$. The results were similar to those presented here. However, the present method of weighing the data allows us to avoid having to arbitrarily exclude of data while still taking into account the relative uncertainties of each datum.