

Near-global distribution of CO isotopic fractionation in the Earth's atmosphere



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ABSTRACT

The first near-global (−85° to 85°) measurements of the isotopic fractionation of ¹³CO relative to ¹²CO have been obtained from 5 to 90 km using the ACE-FTS (Atmospheric Chemistry Experiment-Fourier Transform Spectrometer). These observations have been compared to predictions from WACCM (Whole Atmosphere Community Climate Model). The highest positive fractionation (i.e. relatively more ¹³CO) values of over 100‰ are observed in the lower thermosphere during winter in both hemispheres, whereas the highest negative fractionation (i.e. relatively more ¹²CO) is observed in the mesosphere in the summer at high latitudes (due to the highly fractionating effect that UV light has on CO₂) and year round in the tropics. Agreement between measurements and model results is generally good at high altitude, although ACE shows a stronger fractionation effect from CO₂ photolysis than predicted by WACCM. In the lower atmosphere, agreement is qualitatively good, although there is a distinct discrepancy at 40 km in all seasons, which is likely a retrieval artifact.

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1. Introduction

Carbon monoxide (CO) is an important molecule in atmospheric chemistry. Although it has a small direct global warming potential, it acts as an indirect greenhouse gas as a result of the formation of carbon dioxide (CO₂) through the reaction with the hydroxyl radical (OH). The reaction between CO and OH also leads to the formation of tropospheric ozone (O₃) [1] which acts as both a pollutant and a greenhouse gas [2]. The lifetime of CO (~2 months) makes it an excellent tracer of atmospheric dynamics, in particular vertical transport at high latitudes [3]. Both CO and O₃ are considered major pollutants in the troposphere [4] and have detrimental effects on human health, including lung disease and cancer [5].

CO has four major sources in the troposphere: fossil fuel combustion, biomass burning, methane oxidation and non-methane hydrocarbon oxidation. The major sink throughout the atmosphere is the reaction with OH. Since the concentration of OH is strongly dependent on the actinic flux, and therefore the time of year, the tropospheric lifetime of CO is seasonally variant (1–6 months). The spatial distribution is also varied given the relatively short lifetime and the disparity of fossil fuel production between the Northern and Southern Hemispheres. In the troposphere CO is a

precursor (through production of HO₂) to the formation of ozone under high NO_x conditions [1,6,7]. In the stratosphere and mesosphere the main sources of CO are from formaldehyde (CH₂O), which is formed through hydrocarbon oxidation [8–10], and photodissociation of CO₂, respectively. The volume mixing ratio and lifetime of CO in the mesosphere is much higher than in the troposphere or stratosphere and it can be used as an atmospheric tracer of vertical transport and other dynamical effects in the upper atmosphere.

CO exists predominantly as the ¹²C¹⁶O isotopologue, but there are appreciable amounts of ¹³C¹⁶O in the atmosphere and to a lesser extent ¹²C¹⁷O and ¹²C¹⁸O. The various CO sources have different isotopic signatures [11–13] because of the different isotopic compositions of the reactants and the different fractionation processes that they undergo during CO formation. Indeed removal by OH oxidation also has considerable isotopic fractionation [8]. Measurements of the isotopic makeup of CO can therefore lead to a determination of the various sources and sinks [7,12,14,15]. The variation of the isotopic composition of a sample from the standard isotopic abundance is given in δ notation and expressed as ‘per mil’ (‰) changes. For ¹³C, this would be expressed as

$$\delta^{13}\text{C} = \left[\frac{[^{13}\text{C}_\text{S}]/[^{12}\text{C}_\text{S}]}{[^{13}\text{C}_\text{R}]/[^{12}\text{C}_\text{R}]} - 1 \right] \times 1000\text{‰},$$

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In which the S and R subscripts refer to the concentrations for the sample and reference, respectively. For ^{13}C , this reference is the Vienna Pee Dee Belemnite (V-PDB) which has a $[^{13}\text{C}]/[^{12}\text{C}]$ value of 0.0112372.

A number of previous studies have used CO isotopologues to quantify the relative contributions of the various sources and sinks. In situ collection and measurement of suitable samples can be difficult due to the small volume mixing ratio of CO and generally sophisticated cryogenic traps are used [12] to isolate the sample. This technique is clearly spatially limited, although analysis with mass spectrometry techniques provides highly precise values for the isotopic composition of a sample. Samples from the high latitude northern hemisphere [7], Japan [16], Barbados [14], a transect along the Trans-Siberian railroad [17] and other locales have been analyzed and modeling efforts have included a two dimensional model employed by Manning et al. [15] to predict CO concentrations and $\delta^{13}\text{C}$ values in the extra tropical southern hemisphere. The CARIBIC project has provided isotopic fractionation values for CO in the upper troposphere and lower stratosphere [18], although the sampling method suffered from contamination. However, all of these results are relatively local and cover a limited altitude range. Given the seasonal and spatial variability of CO, as well as the different contributions of sources and sinks, a more comprehensive study is needed. Nadir sounding instruments such as SCIAMACHY [19] and MOPITT [20] and limb sounders such as MIPAS [6], IASI [21] and ACE [22] have successfully measured CO from satellite platforms, although this has not yet been extended to isotopic measurements.

2. Experimental

SCISAT is a Canadian-led satellite mission that was launched in 2003. The primary instrument on board is the Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS) which is a high resolution (0.02 cm^{-1}) spectrometer covering the spectral region $750\text{--}4400\text{ cm}^{-1}$. The instrument records solar occultation spectra, recording transmission spectra through the limb of the Earth's atmosphere at sunrise and sunset over a latitudinal range

of about 85°S to 85°N . The satellite's orbital inclination of 74° provides near global coverage with a strong weighting toward occultations at higher latitudes (Fig. 1). Profiles of over 30 trace gas species are obtained from ACE-FTS spectra, at a vertical resolution of around $3\text{--}4\text{ km}$ [23].

Retrievals of ACE-FTS data were obtained using version 3.5 of the ACE-FTS software [24]. Pressure and temperature profiles are first derived from the ACE-FTS spectra through the analysis of CO_2 lines, and then volume mixing ratio (VMR) profiles are retrieved for the various atmospheric constituents of interest using a forward model in which the target molecule's concentration is adjusted until the calculated spectrum matches observations. Spectroscopic parameters for the forward model calculations were taken from the HITRAN 2004 database [25].

The subsidiary isotopologues from a number of molecules are routinely retrieved from ACE-FTS measurements, including H_2O , CO_2 , O_3 , N_2O , CH_4 , OCS , and CO (<http://www.ace.uwaterloo.ca/>). For carbon monoxide, in addition to the main isotopologue ($^{12}\text{C}^{16}\text{O}$), VMR profiles are retrieved for $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{17}\text{O}$.

The high altitude portion (above $\sim 95\text{ km}$) of the retrieval for main isotopologue CO in version 3.5 differs significantly from version 3.0, the previous processing version. In version 3.0, the CO VMR profile in the thermosphere was assumed to be increasing rapidly with altitude, which yielded an overestimation of the contribution to the calculated spectrum from the altitude region above the highest analyzed measurement ($\sim 110\text{ km}$). In version 3.5, a constant VMR was assumed above the highest analyzed measurement.

The spectral microwindows employed in the CO and ^{13}CO retrievals are presented in Tables 2 and 3, respectively. The ACE-FTS measurements cover the 1–0 and 2–0 CO vibration–rotation bands, both of which are included in the ^{12}CO microwindow set, with the weaker 2–0 band used for low altitudes where many of the lines in the 1–0 band are saturated. The microwindow set for the ^{13}CO isotopologue only contains lines from the fundamental band. Unlike the main isotopologue, lines in the 1–0 band for ^{13}CO do not saturate in the low-altitude ACE-FTS spectra thanks to the lower atmospheric abundance compared to ^{12}CO .

In general, the infrared is well-suited for isotopic studies, containing a wealth of narrow, isolated lines that allows ready

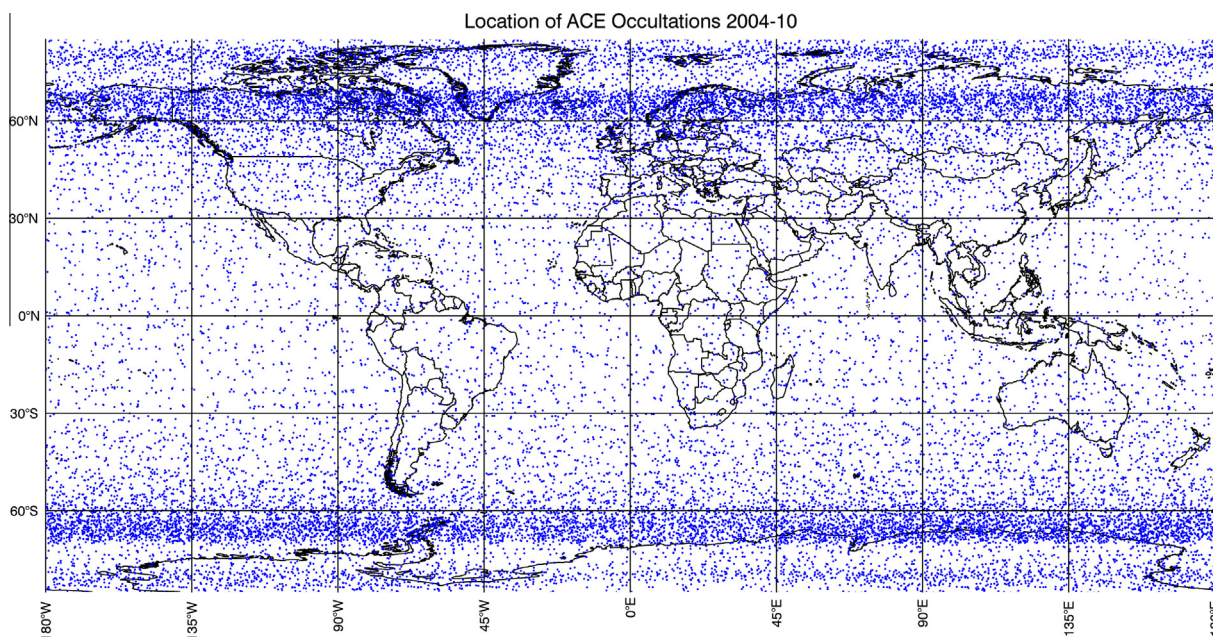


Fig. 1. Locations of 25,855 ACE-FTS occultations between March 2004 and October 2010 showing the global coverage of the instrument with a particularly large number of measurements at high latitudes.

Table 1

The fractionation effects (with respect to V-PDB) of the four main tropospheric CO sources (adapted from Brenninkmeijer et al. [12] and sources therein).

Source	Amount Tg/year	$\delta^{13}\text{C}$ (‰)
Fossil fuel combustion	300–550	–27.5
Biomass burning	300–700	–21.3/–24.5
Methane oxidation	400–1000	–52.6
NMHC oxidation	200–600	–32.2

Table 2

List of microwindows used for ^{12}CO retrievals (ACE-FTS version 3.5 data product).

Center frequency (cm^{-1})	Microwindow width (cm^{-1})	Lower altitude (km)	Upper altitude (km)
1950.10 ^a	0.35	7	15
1986.09 ^a	0.30	6–7	22
2033.08 ^a	0.30	5	8
2046.29	0.24	8	25
2050.90	0.30	20	45
2081.88	0.48	13–15	100
2083.05 ^a	0.70	5	15
2086.36	0.40	15	100
2094.76	0.40	70	110
2098.97	0.50	40	110
2107.46	0.40	60	110
2115.50	0.60	40	110
2119.70	0.50	70	110
2131.65	0.50	18	105
2135.40	1.00	14–16	105
2139.35	1.00	13–15	105
2140.00	1.25	5	22
2140.80 ^a	0.60	5	22
2146.75	1.00	5	22
2147.05	0.90	13–15	105
2149.75 ^a	0.60	5	15
2150.90	0.70	16–17	105
2154.65	0.80	17–18	110
2158.30	0.50	19	110
2161.95	0.50	20	110
2164.00 ^a	0.50	10	20
2165.48	0.55	20	110
2169.13	0.55	20	110
2172.68	0.50	50	110
2176.25	0.45	20	110
2179.85	0.40	60	110
2183.20	0.40	40	110
2186.60	0.40	60	110
4209.38	0.40	5	15
4222.90	0.45	5	15
4227.37	0.70	5	15
4236.01	0.45	5	15
4248.34	0.40	5	15
4274.77	0.30	5	15
4285.10	0.55	5	15

^a Microwindow contains no information on the target. Used to improve the retrieval of interferers.

differentiation between the various isotopologues. Isotopic fractionation of the various isotopologues is often quite small, and so relatively small errors (on the order of a few percent) in spectroscopic line parameters can lead to dramatic errors in δ -values used in isotopologue studies. ^{12}CO and ^{13}CO are retrieved independently as if they are separate molecules and the δ -values are computed at each 1 km altitude. Although CO concentration measurements from ACE have been well validated [3], determination of δ -values as first reported in this paper remain a challenge, mainly because of the quality of the available spectroscopic data.

During the retrievals, VMR profiles for interferers appearing in the CO microwindow set are determined simultaneously. A separate profile is employed for each interfering isotopologue, because different isotopologues of the same molecule generally have different atmospheric profiles. Where the spectral contribution from a particular interferer within the microwindow set is relatively

Table 3

List of microwindows used for ^{13}CO retrievals (ACE-FTS version 3.5 data product).

Center frequency (cm^{-1})	Microwindow width (cm^{-1})	Lower altitude (km)	Upper altitude (km)
1446.50 ^a	0.35	30	50
1649.34 ^a	0.30	20	30
1950.10 ^a	0.35	5–7	20
1977.66 ^a	0.60	5–7	22
1986.09 ^a	0.30	5–7	22
2020.90	0.40	5–8	12
2024.90	0.40	5	12
2033.37	0.30	5	15
2045.67	0.35	12	20
2045.90	0.40	50	85
2049.42	1.00	50	85
2049.92	0.40	12	50
2053.74	0.40	50	85
2057.80	0.30	15	50
2058.05	0.50	50	90
2061.57	0.70	50	90
2061.87	0.35	12	50
2065.82	0.40	50	90
2069.60	0.26	20	90
2073.38	0.55	50	90
2077.45	0.50	60	90
2081.60	1.00	45	90
2084.98	0.40	10	90
2088.77	0.40	45	90
2092.43	0.30	12	20
2103.32	0.40	45	90
2107.15	0.70	55	90
2111.00	1.25	50	90
2113.95	0.40	50	90
2117.35	0.35	55	90
2120.90	0.35	55	90
2124.00	0.80	60	90
2127.65	0.30	60	90
2131.34	1.00	40	90
2134.35	0.35	45	90
2137.60	0.30	5–7	85
2140.80	0.60	5	40
2144.10	0.40	5	45
2147.10	0.40	20	40
2153.28	0.45	5	12
2159.60	0.40	5–7	12

^a Microwindow contains no information on the target. Used to improve the retrieval of interferers.

weak, additional microwindows are employed that contain information primarily from the interferer, rather than from the target CO isotopologue. If the spectral content from a particular interferer is too meager, it can compromise the convergence stability of the least squares analysis. For the main isotopologue, the interferers in the version 3.5 microwindow set were H_2^{16}O , H_2^{17}O , CO_2 , $^{18}\text{O}^{12}\text{C}^{16}\text{O}$, $^{17}\text{O}^{12}\text{C}^{16}\text{O}$, O_3 , $^{18}\text{O}^{16}\text{O}^{16}\text{O}$, N_2O , ^{15}NNO , N^{15}NO , ^{13}CO , C^{18}O , CH_4 , and OCS . For ^{13}CO , the interferers were H_2^{16}O , H_2^{18}O , H_2^{17}O , CO_2 , $^{13}\text{CO}_2$, $^{18}\text{O}^{12}\text{C}^{16}\text{O}$, $^{17}\text{O}^{12}\text{C}^{16}\text{O}$, O_3 , $^{18}\text{O}^{16}\text{O}^{16}\text{O}$, $^{16}\text{O}^{18}\text{O}^{16}\text{O}$, $^{17}\text{O}^{16}\text{O}^{16}\text{O}$, $^{16}\text{O}^{17}\text{O}^{16}\text{O}$, N_2O , ^{12}CO , C^{18}O , CH_4 , and OCS .

ACE measurements of the main isotopologue ($^{12}\text{C}^{16}\text{O}$) from the 2.2 version dataset have been extensively compared with other satellite missions as well as airborne and ground based products in Clerbaux et al. [3] and the retrieval errors were found to be within 5% from the upper troposphere to 40 km and 10% above 40 km. The CO data product in version 3.0 differs from version 2.2 with small changes in the lower and mid stratosphere [26] and version 3.5 differs from version 3.0 at much higher altitudes, as mentioned previously. With the validation [3] and corrections from subsequent dataset versions ACE has been shown to be a viable platform for CO measurements in the atmosphere from 8 to 110 km. The ^{13}CO retrieval has not been validated yet.

The Whole Atmosphere Community Climate Model (WACCM) version 4 is a component of the Community Earth System Model

Table 4

List of major reactions for CO in the atmosphere with their related kinetic isotope effects k_{12}/k_{13} . All KIEs for the chemical reactions are reported at 298 K and 1 atmosphere pressure. CO₂ photolysis is reported at 295 K.

Reactants	Products	k_{12}/k_{13}	Source
CH ₄ + OH	CH ₃ O ₂ + H ₂ O	1.00288	[41]
CH ₃ Cl + Cl	HO ₂ + CO + 2HCl	1.07	[42]
CH ₂ O + NO ₃	CO + HO ₂ + HNO ₃	0.96	[9]
CH ₂ O + OH	CO + H ₂ O + H	0.952	[9]
CH ₂ O + Br	HBr + HO ₂ + CO	1.13	[9]
CH ₂ O + Cl	HCl + HO ₂ + CO	1.058	[9]
CO + OH + M	CO ₂ + HO ₂ + M	1.00597	[43]
CO ₂ + hν	CO + O	Varies	[28,29]

[27] which includes fully interactive chemistry and dynamics. Here, we use WACCM as a standalone model with a resolution of 4° latitude by 5° with 66 vertical levels from the surface to 5×10^{-6} hPa, which is approximately 140 km, wholly covering the ACE vertical acquisition range for ¹²CO and ¹³CO. WACCM was run for 20 years from initial conditions in the year 2000, with the final three being used for analysis.

Although WACCM does not specifically support molecular isotopologues, different isotopologues may be analyzed as separate species, with the rate constants for their reactions adjusted for the kinetic isotope effects. The kinetic isotope effects for the major reactions in the WACCM input are given in Table 4. Although some of these reactions show temperature and/or pressure dependence [12], the KIEs were inserted into the model as constants. This is expected to cause a small but increasing amount of error at higher altitudes where pressure and temperature decrease. In addition, the photolysis of CO₂ is the major source of CO at high altitudes and each isotopologue has a different absorption cross section for a given wavelength. At wavelengths above 150 nm, theoretical values for each isotopologue's cross section are used [28]. Below 150 nm, where theoretical cross sections were not calculated, experimental values [29] for ¹²C¹⁶O are used for both isotopologues. Isotopic differences for other photochemical reactions were not included.

Lower boundary conditions representing surface emissions were added to WACCM for CO and ¹³CO. Boundary conditions for CH₄ and CO₂ are already present in the model, so these two molecules were modified to include their heavy isotopologues. Data for

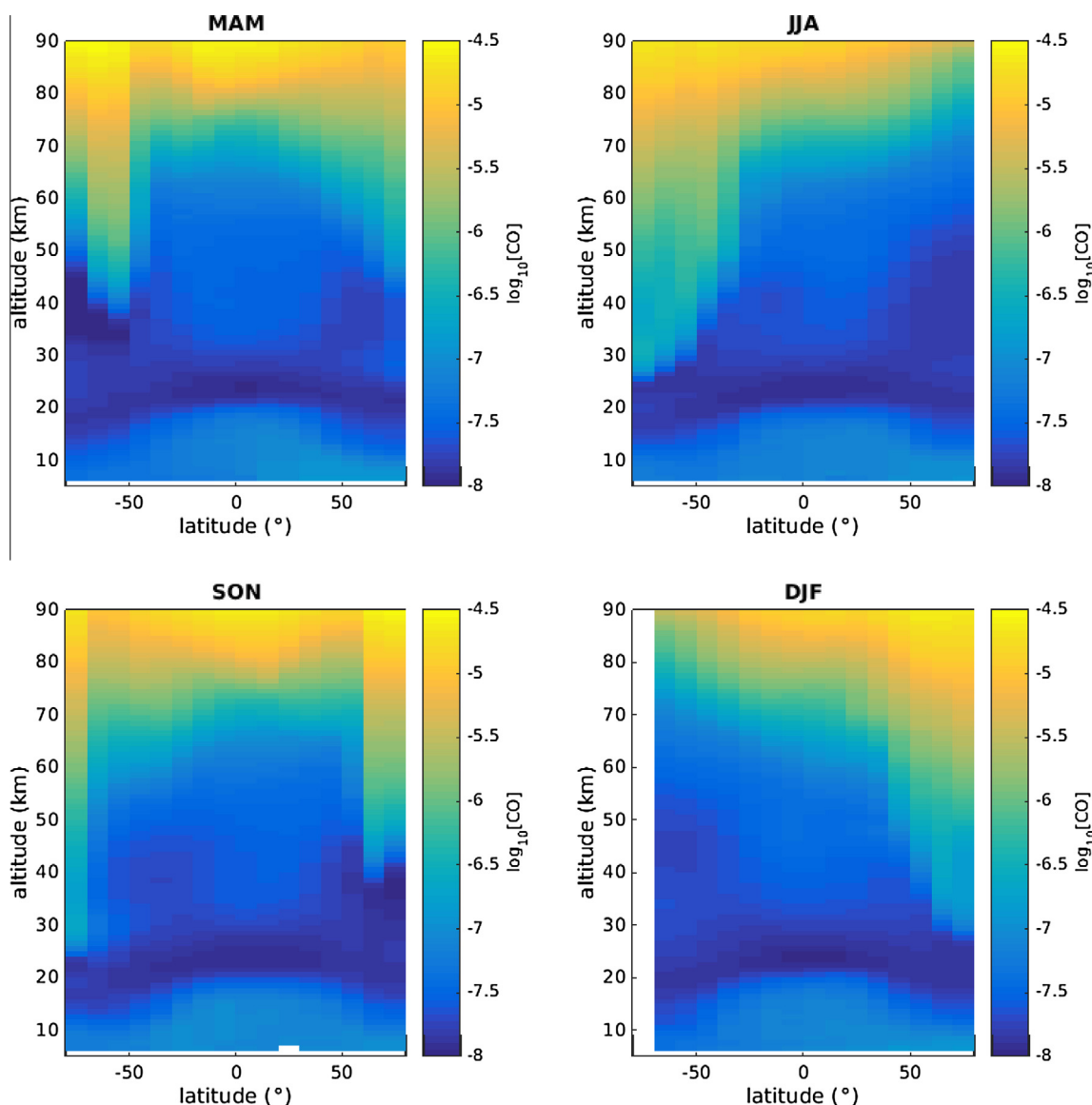


Fig. 2. Seasonal variation in CO VMR as a function of latitude between 8 and 90 km. The colder and therefore denser air, traced by CO formed by CO₂ photolysis (high VMR), in each hemisphere's respective winter can be seen to descend to lower altitudes.

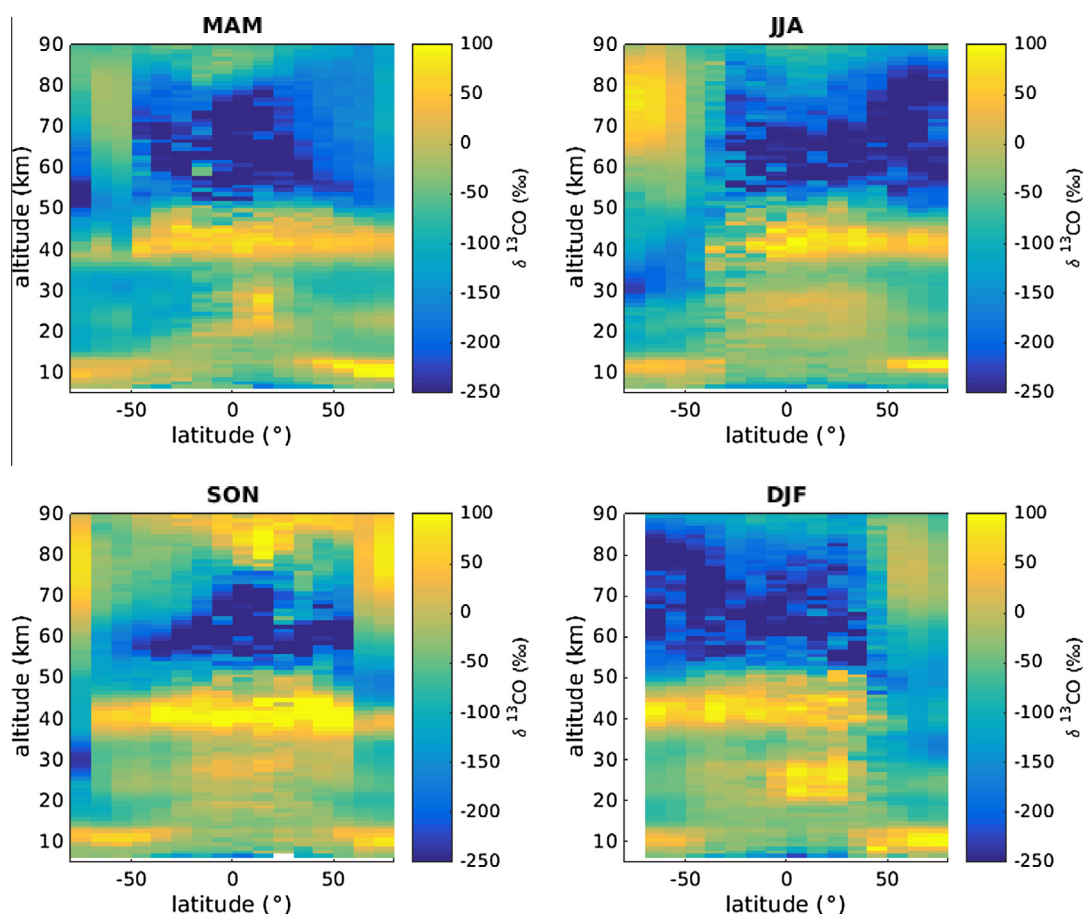


Fig. 3. Seasonal variation of $\delta^{13}\text{CO}$ as a function of latitude between 8 and 90 km from the ACE-FTS.

surface CO concentrations were collected from the NOAA ESRL Carbon Cycle Cooperative Global Air Sampling Network [30] and interpolated over all latitudes. The boundary conditions for ^{13}CO were calculated using $\delta^{13}\text{C}$ measurements from the work of Bergamaschi et al. [31]. Data from the Northern and Southern hemisphere were averaged separately. For CH_4 and CO_2 , the following $[\text{CH}_4] - \delta^{13}\text{C}$ and $[\text{CO}_2] - \delta^{13}\text{C}$ relations were derived from experimental data by Röckmann et al. [32], and Assonov et al. [33],

$$\delta^{13}\text{C}(\text{CH}_4)/\text{‰} = \frac{1.29 \times 10^4}{[\text{CH}_4]/(\text{ppm})} - 151.4$$

$$\delta^{13}\text{C}(\text{CO}_2)/\text{‰} = \frac{6.47 \times 10^3}{[\text{CO}_2]/(\text{ppm})} - 25.3.$$

These relations were combined with WACCM's out-of-the-box boundary condition data [34] to calculate boundary conditions for each isotopologue.

3. Results and discussion

A total of 25,855 occultations containing concentrations of ^{12}CO and ^{13}CO were successfully obtained. Physically unrealistic data are removed from the data product of the obtained occultations. Quality flags are assigned to the data based on a statistical fitting and outliers, which may be due to instrumental or processing errors [35]; these quality flags are available as part of the ACE data products. Data with quality flags of 1 were accepted, individual data with quality flags of 2 or greater, or any occultation containing any data with quality flags of 4, 5 or 6 were rejected. The accepted

occultations are grouped into one of eighteen 10° latitude bins. The data are further binned by altitude (1 km bins). The global distribution of the total concentration of CO by season can be seen in Fig. 2, where MAM refers to March, April and May, JJA refers to June, July and August, SON refers to September, October, November and DJF refers to December, January and February. The $\delta^{13}\text{CO}$ values from ACE are calibrated by comparing subtropical values at 8–10 km with $\delta^{13}\text{CO}$ values at the same latitude and altitude from aircraft transects in the troposphere obtained by Mak and Brenninkmeijer [36]. A calibration factor of 0.99582 was applied to the ACE ^{13}CO concentrations in order to match the satellite and in situ $\delta^{13}\text{CO}$ values. This factor is likely due to a small inconsistency between the ^{12}CO and ^{13}CO line intensities. VMRs of around 100 ppb in the troposphere, decreasing to between 20 and 50 ppb in the stratosphere can be seen and these results are consistent with previous satellite measurements [3]. The large production by photolysis of CO_2 at high altitudes can clearly be seen, as can the dynamics of the air masses between the seasons. Another interesting feature is the asymmetrical distribution of CO between the Northern and Southern Hemispheres in the troposphere, with higher CO concentrations in the Northern Hemisphere being expected because of the larger emissions and in situ formation.

There is a distinct hemispheric and seasonal disparity in the distribution of CO in the atmosphere (Fig. 2). This is caused by atmospheric dynamics, specifically the upwelling of tropical air (Brewer–Dobson circulation) and the downwelling of air from the upper mesosphere and thermosphere in the polar regions in the winter. This effect can be seen more clearly in our WACCM results, including an animation of monthly CO concentrations. The effect of this is that during winter months, CO from UV photol-

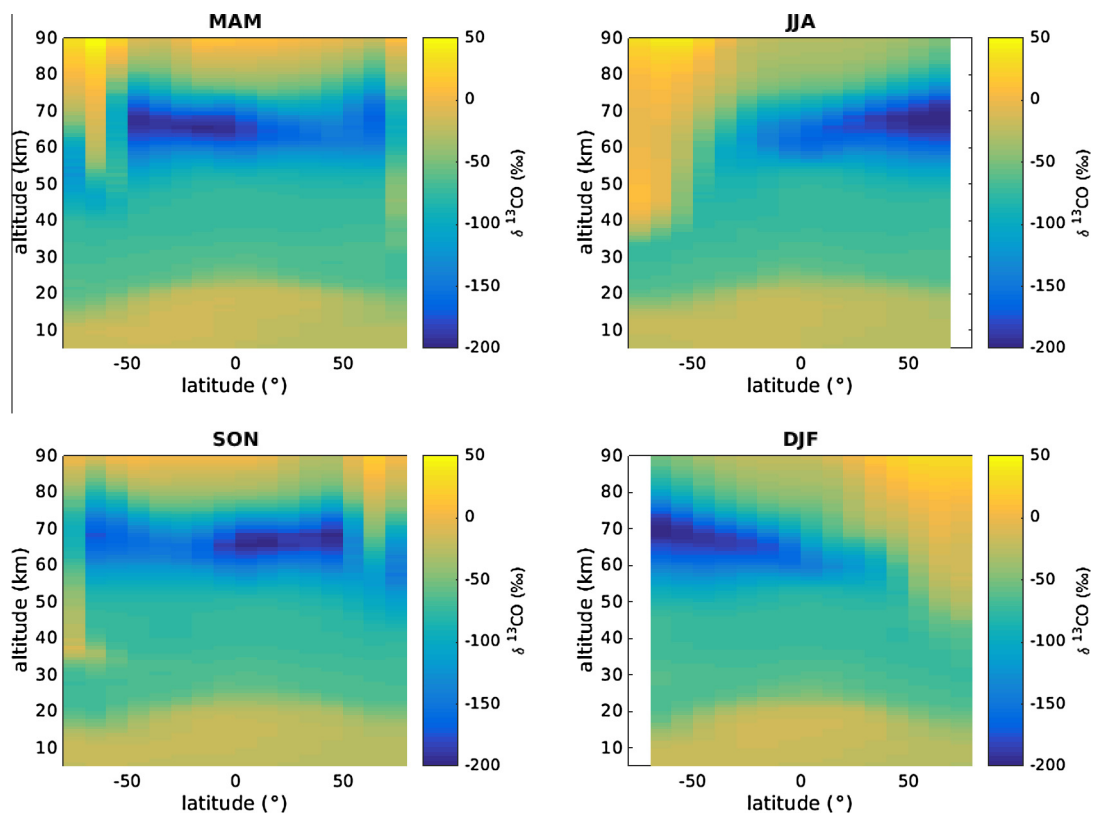


Fig. 4. Seasonal variation of $\delta^{13}\text{CO}$ as a function of latitude between 0 and 90 km from WACCM.

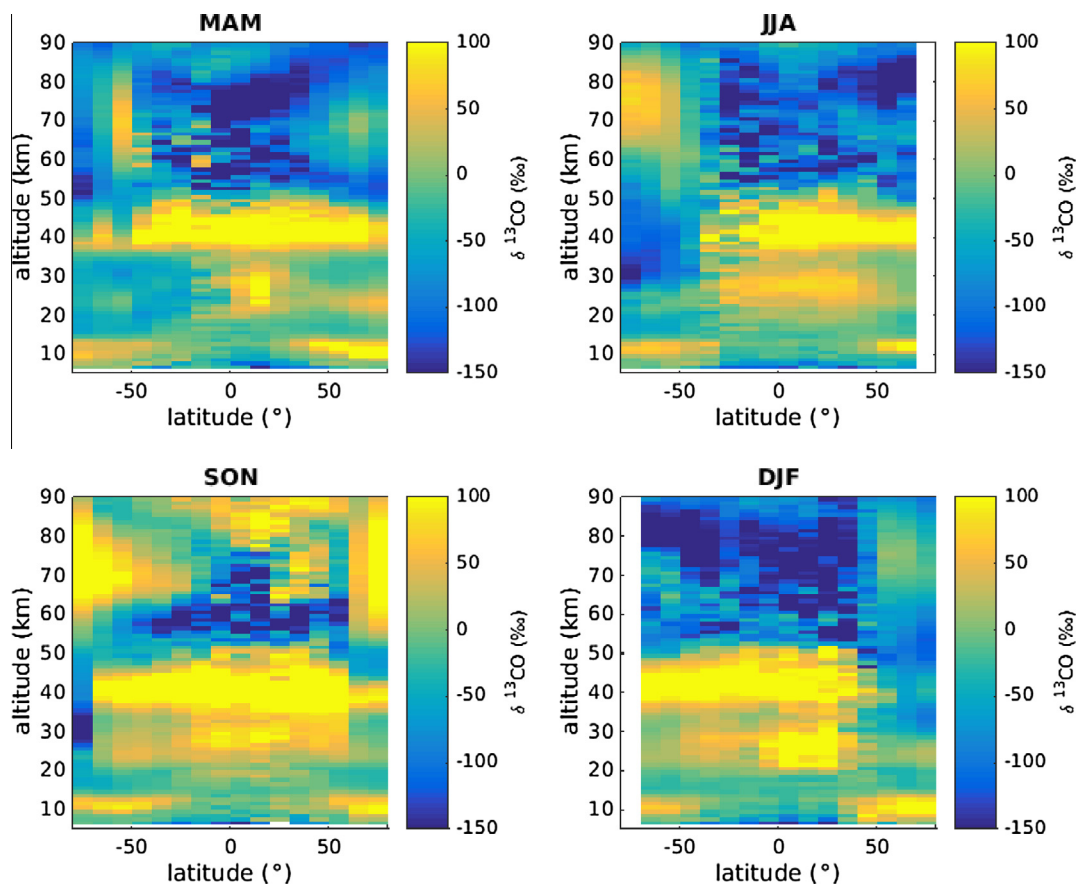


Fig. 5. Difference between ACE measurements of $\delta^{13}\text{CO}$ and WACCM output.

ysis of CO₂ in the thermosphere descends into the stratosphere where the concentration of CO at a particular altitude is higher than other latitudes by a factor of ten or more. Ground-based FTIR measurements [37] show the rapid change of CO column densities by season with increased CO in the winter in each hemisphere with the greatest changes coming at high latitudes.

Fig. 3 shows how the isotopic fractionation of ¹³CO varies by season. The bands of highly positive fractionation near 10 km and 40–50 km are most likely due to systematic errors in the CO VMR retrievals in the vicinity of those altitudes. Although seemingly a problem, these results highlight the sensitivity of our method. The individual atmospheric concentration profiles of CO isotopologues from the ACE-FTS [3] do not show any glaring errors, but this analysis shows that isotopic fractionation can be used to diagnose problems in the retrievals from satellite observations. Although the VMR of formaldehyde (CH₂O) peaks in the troposphere and at around 40 km [38,39] which could explain a slight positive fractionation as oxidation of formaldehyde favors ¹³CO production over ¹²CO [9]. However, the apparent enhanced fractionation near 40 km seen in Fig. 3 is very high, exhibits a suspiciously flat variation with latitude, and no such feature is seen in our WACCM results, all of which suggests that the feature is an artifact.

The positive fractionation observed at 20–30 km, just above the tropical and subtropical tropopause, is another noticeable feature in all seasons. Perhaps this positive fractionation is indicative of the reaction of CO with OH, which will fractionate the air mass by preferentially removing the lighter isotope and therefore the remaining CO has a higher relative abundance of ¹³CO. This kinetic isotope effect has a small positive value of 5‰ [12] (Table 4). Outside of the tropics and sub tropics, the CO has the fractionation signature of that created by the oxidation of methane of −52.5‰ (Table 1). This latitudinal dependence is not observed in WACCM, where the entire stratosphere has the isotopic signature of CO formed by the oxidation of methane. Unlike the features at 40 km, the observations in the tropics do not exhibit features that are typical of a retrieval error and we suspect that these results show a real fractionation effect in the atmosphere not modeled by WACCM. Indeed, the concentrations of CO in the atmosphere are at their lowest in this region (Fig. 2) so it is expected that the isotopic signature of CO in the tropics will be highly dependent on its oxidation by OH.

The fractionation of CO isotopologues in the mesosphere varies spatially and seasonally; in general the values are highly negative around 60 km and positive at 80 km and higher. CO at high altitudes is primarily formed from photolysis of CO₂. Photolysis of CO₂ from UV light between 167 nm and 210 nm is the main source of CO in the mesosphere and lower thermosphere (MLT) [28]. This photolysis has a very high fractionation effect and given the increase of UV radiation in the respective summers, explains the highly negative values in the MLT shown in Fig. 3 in the summer, where the air is subjected to UV radiation and therefore photolysis. Indeed, in a simulated photolysis experiment Schmidt et al. [28] found ¹²CO₂ to photolyze much faster than ¹³CO₂, leading to ¹²CO enrichment, in agreement with ACE observations. However, downwelling from the thermosphere in the winter results in CO that is enriched in ¹³CO (positive δ value) to descend into the mesosphere and even in the upper stratosphere as seen in the southern hemisphere in JJA and the northern hemisphere in DJF (Fig. 1). In the winter, the air at these latitudes is subject to much less photolysis as it receives little sunlight and as a result the highly negative fractionation observed in other seasons does not occur.

WACCM results in Fig. 4 generally represent the observed data well. The tropospheric values are consistent with in situ measurements [7,14,16] and are less variable than the ACE-FTS data at low altitudes. The observed fractionation at 40–50 km is not seen in

Fig. 4, but the evidence of the effect of dynamics (which WACCM includes) on the distribution of CO fractionation is. As with CO concentrations, this is best viewed as a month by month animation, but winter descent as part of the polar vortex can be seen in the upper right and lower right panels of Fig. 4. Although the trend of fractionation is similar to ACE-FTS results, the strength of fractionation is different between the two results with ACE results showing much higher depletion of ¹³CO in the lower and middle mesosphere. Fig. 5 shows the difference between $\delta^{13}\text{CO}$ determined from ACE measurements and WACCM. From 15 to 37 km, outside of the tropics, these residuals are close to zero, however the band of high fractionation at 40–50 km and the smaller positive fractionation in the tropical stratosphere at 20–30 km, which were not shown from WACCM, are highlighted in Fig. 5. The residuals in the mesosphere show that our WACCM runs underestimate fractionation in that region of the atmosphere. Although our treatment of CO₂ photolysis is not comprehensive, due to the fact that isotopic dependent cross sections are not available for all wavelengths, appropriate cross sections have been used where possible. We believe this first attempt to model ¹³CO in the atmosphere to be at least semi-quantitative. Indeed the differences between WACCM and ACE shown in Fig. 5 at high altitudes may be due to our inability to implement correct cross section data below 150 nm or at the appropriate temperatures or pressures.

There have been a number of studies of CO isotopic fractionation on the surface of the Earth. ACE has coverage of CO in the troposphere, although spectral congestion in the low atmosphere results in measurements at the surface being less accurate than those higher in the troposphere. As the troposphere is relatively well mixed, ACE $\delta^{13}\text{CO}$ values from the higher troposphere may be compared to surface measurements. In the sub tropics, the average $\delta^{13}\text{CO}$ value from ACE in the troposphere is −32‰. Measurements from Mount Sonnblick, Austria (47°N) have $\delta^{13}\text{CO}$ values ranging between −25 and −30‰, [40], from Happono, Japan (37°N) have values between −24‰ and −29‰ [16] and a transect across the Trans-Siberian Railroad had values ranging between −26‰ and −29.5‰ [17].

4. Conclusion

We present the first near global atmospheric data set of the isotopic fractionation of CO based on infrared remote sensing measurements from orbit. The advantage of measuring the various isotopologues of CO is that δ values identify the particular chemical or physical source. Our satellite observations and model results show the high concentrations of ¹³CO in winter to have descended from the thermosphere. The good agreement between observation and model results show that ACE instrument is a useful tool to study the seasonal variation in atmospheric dynamics and may be used to analyze the isotope chemistry of the upper atmosphere.

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References

- [1] M. Pommier, K.S. Law, C. Clerbaux, S. Turquety, D. Hurtmans, J. Hadji-Lazaro, P. F. Coheur, H. Schlager, G. Ancellet, J.D. Paris, P. Nédélec, G.S. Diskin, J.R. Podolske, J.S. Holloway, P. Bernath, *Atmos. Chem. Phys.* 10 (2010) 10655–10678.
- [2] B.J. Finlayson-Pitts, J.N. Pitts, *Science* 276 (1997) 1045–1051.
- [3] C. Clerbaux, M. George, S. Turquety, K.A. Walker, B. Barret, P. Bernath, C. Boone, T. Borsdorff, J.P. Cammas, V. Catoire, M. Coffey, P.F. Coheur, M. Deeter, M. De Mazière, J. Drummond, P. Duchatelet, E. Dupuy, R. de Zafra, F. Eddounia, D.P. Edwards, L. Emmmons, B. Funke, J. Gille, D.W.T. Griffith, J. Hannigan, F. Hase, M. Höpfner, N. Jones, A. Kagawa, Y. Kasai, I. Kramer, E. Le Flochmoën, N.J. Livesey,

- M. López-Puertas, M. Luo, E. Mahieu, D. Murtagh, P. Nédélec, A. Pazmino, H. Pumphrey, P. Ricaud, C.P. Rinsland, C. Robert, M. Schneider, C. Senten, G. Stiller, A. Strandberg, K. Strong, R. Sussmann, V. Thouret, J. Urban, A. Wiacek, *Atmos. Chem. Phys.* 8 (2008) 2569–2594.
- [4] D. Parrish, Carbon monoxide and light alkanes as tropospheric tracers of anthropogenic ozone, in: H. Niki, K.H. Becker (Eds.), *The Tropospheric Chemistry of Ozone in the Polar Regions*, Springer, Berlin Heidelberg, 1993, pp. 155–169.
- [5] K.L. Ebi, G. McGregor, *Environ. Health Perspect.* 116 (2008) 1449–1455.
- [6] B. Funke, M. López-Puertas, M. García-Comas, G.P. Stiller, T. von Clarmann, M. Höpfner, N. Glatthor, U. Grabowski, S. Kellmann, A. Linden, *Atmos. Chem. Phys.* 9 (2009) 2387–2411.
- [7] T. Röckmann, P. Jöckel, V. Gros, M. Bräunlich, G. Possnert, C.A.M. Brenninkmeijer, *Atmos. Chem. Phys.* 2 (2002) 147–159.
- [8] K.L. Feilberg, M.S. Johnson, C.J. Nielsen, *Phys. Chem. Chem. Phys.* 7 (2005) 2318–2323.
- [9] K.L. Feilberg, M.S. Johnson, C.J. Nielsen, *J. Phys. Chem. A* 108 (2004) 7393–7398.
- [10] K.L. Feilberg, B. D'Anna, M.S. Johnson, C.J. Nielsen, *J. Phys. Chem. A* 109 (2005) 8314–8319.
- [11] V. Gros, P. Jöckel, C.A.M. Brenninkmeijer, T. Röckmann, F. Meinhardt, R. Graul, *Atmos. Environ.* 36 (2002) 2831–2840.
- [12] C.A.M. Brenninkmeijer, T. Röckmann, M. Bräunlich, P. Jöckel, P. Bergamaschi, *Chemosphere – Glob. Change Sci.* 1 (1999) 33–52.
- [13] Z. Wang, J. Chappellaz, P. Martinerie, K. Park, V. Petrenko, E. Witrant, L.K. Emmons, T. Blunier, C.A.M. Brenninkmeijer, J.E. Mak, *Atmos. Chem. Phys.* 12 (2012) 4365–4377.
- [14] J.E. Mak, G. Kra, T. Sandomenico, P. Bergamaschi, *J. Geophys. Res.: Atmos.* 108 (2003) 4635.
- [15] M.R. Manning, C.A.M. Brenninkmeijer, W. Allan, *J. Geophys. Res.: Atmos.* 102 (1997) 10673–10682.
- [16] S. Kato, Y. Kajii, H. Akimoto, M. Bräunlich, T. Röckmann, C.A.M. Brenninkmeijer, *J. Geophys. Res.: Atmos.* 105 (2000) 8891–8900.
- [17] O.A. Tarasova, C.A.M. Brenninkmeijer, S.S. Asonov, N.F. Elansky, T. Röckmann, M.A. Sofiev, *J. Atmos. Chem.* 57 (2007) 135–152.
- [18] S. Gromov, C.A.M. Brenninkmeijer, *Atmos. Chem. Phys.* 15 (2015) 1901–1912.
- [19] A.T.J. de Laat, A.M.S. Gloudemans, H. Schrijver, M.M.P. van den Broek, J.F. Meirink, I. Aben, M. Krol, *Geophys. Res. Lett.* 33 (2006) L07807.
- [20] M.N. Deeter, L.K. Emmons, G.L. Francis, D.P. Edwards, J.C. Gille, J.X. Warner, B. Khattatov, D. Ziskin, J.F. Lamarque, S.P. Ho, V. Yudin, J.L. Attié, D. Packman, J. Chen, D. Mao, J.R. Drummond, *J. Geophys. Res.: Atmos.* 108 (2003) 4399.
- [21] M. George, C. Clerbaux, D. Hurtmans, S. Turquety, P.F. Coheur, M. Pommier, J. Hadji-Lazaro, D.P. Edwards, H. Worden, M. Luo, C. Rinsland, W. McMillan, *Atmos. Chem. Phys.* 9 (2009) 8317–8330.
- [22] C. Clerbaux, P.F. Coheur, D. Hurtmans, B. Barret, M. Carleer, R. Colin, K. Semeniuk, J.C. McConnell, C. Boone, P. Bernath, *Geophys. Res. Lett.* 32 (2005) L16S01.
- [23] P.F. Bernath, C.T. McElroy, M.C. Abrams, C.D. Boone, M. Butler, C. Camy-Peyret, M. Carleer, C. Clerbaux, P.F. Coheur, R. Colin, P. DeCola, M. DeMazière, J.R. Drummond, D. Dufour, W.F.J. Evans, H. Fast, D. Fussen, K. Gilbert, D.E. Jennings, E.J. Llewellyn, R.P. Lowe, E. Mahieu, J.C. McConnell, M. McHugh, S.D. McLeod, R. Michaud, C. Midwinter, R. Nassar, F. Nichitiu, C. Nowlan, C.P. Rinsland, Y.J. Rochon, N. Rowlands, K. Semeniuk, P. Simon, R. Skelton, J.J. Sloan, M.A. Soucy, K. Strong, P. Tremblay, D. Turnbull, K.A. Walker, I. Walkty, D.A. Wardle, V. Wehrle, R. Zander, J. Zou, *Geophys. Res. Lett.* 32 (2005) L15S01.
- [24] C.D. Boone, K.A. Walker, P.F. Bernath, Version 3 retrievals for the atmospheric chemistry experiment Fourier transform spectrometer (ACE-FTS), in: P.F. Bernath (Ed.), *The Atmospheric Chemistry Experiment ACE at 10: A Solar Occultation Anthology*, A. Deepak Publishing, Hampton, Virginia, USA, 2013, pp. 103–127.
- [25] L.S. Rothman, D. Jacquemart, A. Barbe, D. Chris Benner, M. Birk, L.R. Brown, M. R. Carleer, C. Chackerian Jr., K. Chance, L.H. Coudert, V. Dana, V.M. Devi, J.M. Flaud, R.R. Gamache, A. Goldman, J.M. Hartmann, K.W. Jucks, A.G. Maki, J.Y. Mandin, S.T. Massie, J. Orphal, A. Perrin, C.P. Rinsland, M.A.H. Smith, J. Tennyson, R.N. Tolchenov, R.A. Toth, J. Vander Auwera, P. Varanasi, G. Wagner, *J. Quant. Spectrosc. Radiat. Transfer* 96 (2005) 139–204.
- [26] C. Waymark, K. Walker, C. Boone, E. Dupuy, P. Bernath, *Imaging and Applied Optics*, Optical Society of America, Toronto, 2011, p. FMB4.
- [27] D.R. Marsh, M.J. Mills, D.E. Kinnison, J.-F. Lamarque, N. Calvo, L.M. Polvani, *J. Clim.* 26 (2013) 7372–7391.
- [28] J.A. Schmidt, M.S. Johnson, R. Schinke, *Proc. Natl. Acad. Sci. USA* 110 (2013) 17691–17696.
- [29] K. Yoshino, J.R. Esmond, Y. Sun, W.H. Parkinson, K. Ito, T. Matsui, *J. Quant. Spectrosc. Radiat. Transfer* 55 (1996) 53–60.
- [30] P. Novelli, K. Masarie, <ftp://aftp.cmdl.noaa.gov/data/trace_gases/co/flask/surface/README_surface_flask_co.html>, 2014.
- [31] P. Bergamaschi, R. Hein, C.A.M. Brenninkmeijer, P.J. Crutzen, *J. Geophys. Res.: Atmos.* 105 (2000) 1929–1945.
- [32] T. Röckmann, M. Brass, R. Borchers, A. Engel, *Atmos. Chem. Phys.* 11 (2011) 13287–13304.
- [33] S.S. Asonov, C.A.M. Brenninkmeijer, T.J. Schuck, P. Taylor, *Atmos. Chem. Phys.* 10 (2010) 8575–8599.
- [34] J.F. Lamarque, T.C. Bond, V. Eyering, C. Granier, A. Heil, Z. Klimont, D. Lee, C. Liousse, A. Mieville, B. Owen, M.G. Schultz, D. Shindell, S.J. Smith, E. Stehfest, J. Van Aardenne, O.R. Cooper, M. Kainuma, N. Mahowald, J.R. McConnell, V. Naik, K. Riahi, D.P. van Vuuren, *Atmos. Chem. Phys.* 10 (2010) 7017–7039.
- [35] P.E. Sheese, C.D. Boone, K.A. Walker, *Atmos. Meas. Tech.* 8 (2015) 741–750.
- [36] J.E. Mak, C.A.M. Brenninkmeijer, *J. Geophys. Res.: Atmos.* 103 (1998) 19347–19358.
- [37] V. Velazco, S.W. Wood, M. Sinnhuber, I. Kramer, N.B. Jones, Y. Kasai, J. Notholt, T. Warneke, T. Blumenstock, F. Hase, F.J. Murcray, O. Schrems, *Atmos. Chem. Phys.* 7 (2007) 1305–1312.
- [38] C. Vigouroux, F. Hendrick, T. Stavrou, B. Dils, I. De Smedt, C. Hermans, A. Merlaud, F. Scolas, C. Senten, G. Vanhaelewyn, S. Fally, M. Carleer, J.M. Metzger, J.F. Müller, M. Van Roozendael, M. De Mazière, *Atmos. Chem. Phys.* 9 (2009) 9523–9544.
- [39] P. Ricaud, D. Alexandre, B. Barret, E. Le Flochmoën, E. Motte, G. Berthet, F. Lefèvre, D. Murtagh, *J. Quant. Spectrosc. Radiat. Transfer* 107 (2007) 91–104.
- [40] V. Gros, M. Bräunlich, T. Röckmann, P. Jöckel, P. Bergamaschi, C.A.M. Brenninkmeijer, W. Rom, W. Kutschera, A. Kaiser, H.E. Scheel, M. Mandl, J. van der Plicht, G. Possnert, *J. Geophys. Res.: Atmos.* 106 (2001) 3179–3193.
- [41] S.P. Sander, J. Abbatt, J.R. Barker, J.B. Burkholder, R.R. Friedl, D.M. Golden, R.E. Huie, C.E. Kolb, M.J. Kurylo, G.K. Moortgat, V.L. Orkin, P.H. Wine, *JPL Publication 10-6*, Jet Propulsion Laboratory, Pasadena, 2011.
- [42] A.A. Gola, B. D'Anna, K.L. Feilberg, S.R. Sellevåg, L. Bache-Andreassen, C.J. Nielsen, *Atmos. Chem. Phys.* 5 (2005) 2395–2402.
- [43] T. Röckmann, C.A.M. Brenninkmeijer, G. Saueressig, P. Bergamaschi, J.N. Crowley, H. Fischer, P.J. Crutzen, *Science* 281 (1998) 544–546.