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

C.A. Beale a,⁎, E.M. Buzan b, C.D. Boone c, P.F. Bernath b,c

a Department of Ocean, Earth and Atmospheric Sciences, Old Dominion University, Norfolk, VA 23529, United States
b Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529, United States
c Department of Chemistry, University of Waterloo, Waterloo, ON N2L 3G1, Canada

⁎ Corresponding author.
E-mail address: cbeale@odu.edu (C.A. Beale).

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 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

\[ \delta^{13}C = \left( \frac{\text{[13C]}}{\text{[12C]}} \right) \times 1000 \ \text{‰} \]
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 $^{[13]}$C/$^{[12]}$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 $\delta^{13}$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 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 750–4400 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 3–4 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$_2$O, CO$_2$, O$_3$, N$_2$O, CH$_4$, OCS, and CO (http://www.ace.uwaterloo.ca/). For carbon monoxide, in addition to the main isotopologue (12C16O), VMR profiles are retrieved for 13C16O, 12C18O and 12C17O.

The high altitude portion (above ~95 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 (~110 km). In version 3.5, a constant VMR was assumed above the highest analyzed measurement. The spectral microwindows employed in the CO and 13CO 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 12CO 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 13CO isotopologue only contains lines from the fundamental band. Unlike the main isotopologue, lines in the 1–0 band for 13CO do not saturate in the low-altitude ACE-FTS spectra thanks to the lower atmospheric abundance compared to 12CO.

In general, the infrared is well-suited for isotopic studies, containing a wealth of narrow, isolated lines that allows ready
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 analyses. For the main isotopologue, the interferers in the version 3.5 microwindow set were H2, CH4, and OCS.

During the retrievals, VMR profiles for interferers appearing in the CO microwindow set are determined simultaneously. If the spectral content from a particular interferer within the microwindow set is relatively small, 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 analyses. For the main isotopologue, the interferers in the version 3.5 microwindow set were H2, CH4, and OCS. For 13CO, the interferers were H2, CH4, and OCS. For 13CO, the interferers were H2, CH4, and OCS.
which includes fully interactive chemistry and dynamics. Here, we use WACCM as a standalone model with a resolution of 4°C176 latitude by 5°C176 with 66 vertical levels from the surface to 5°C2106 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

<table>
<thead>
<tr>
<th>Reactants Products</th>
<th>$k_{12}/k_{13}$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4 + OH</td>
<td>CH2O + H2O</td>
<td>1.00288</td>
</tr>
<tr>
<td>CH2Cl + Cl</td>
<td>HCl + CO + 2HCl</td>
<td>1.07</td>
</tr>
<tr>
<td>CH3O + NO2</td>
<td>CO + HO2 + HNO3</td>
<td>0.96</td>
</tr>
<tr>
<td>CH3O + OH</td>
<td>CO + HO2 + H</td>
<td>0.952</td>
</tr>
<tr>
<td>CH3O + Br</td>
<td>HBr + HO2 + CO</td>
<td>1.13</td>
</tr>
<tr>
<td>CH3O + Cl</td>
<td>HCl + HO2 + CO</td>
<td>1.058</td>
</tr>
<tr>
<td>CO + OH + M</td>
<td>CO2 + HO2 + M</td>
<td>1.00597</td>
</tr>
<tr>
<td>CO2 + hv</td>
<td>CO + O</td>
<td>Varies</td>
</tr>
</tbody>
</table>

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.

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.
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 $\delta^{13}$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 $[\text{CH}_4] - \delta^{13}$C and $[\text{CO}_2] - \delta^{13}$C relations were derived from experimental data by Röckmann et al. [32], and Assonov et al. [33],

$$\delta^{13}$C(CH$_4$)/‰ $=$ $0.29 \times 10^4$ (ppm) $-$ 151.4
$$\delta^{13}$C(CO$_2$)/‰ $=$ $6.47 \times 10^3$ (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 $\delta^{13}$CO values from ACE are calibrated by comparing subtropical values at 8–10 km with $\delta^{13}$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 $\delta^{13}$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 $\delta^{13}$CO as a function of latitude between 0 and 90 km from WACCM.

Fig. 5. Difference between ACE measurements of $\delta^{13}$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 12CO production over 13CO [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 12CO. 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. Photoysis 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 12CO to photolyze much faster than 13CO, 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 δ13CO 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 δ13CO values from the higher troposphere may be compared to surface measurements. In the sub tropics, the average δ13CO value from ACE in the troposphere is ~32‰. Measurements from Mount Sonnblick, Austria (47°N) have δ13CO values ranging between ~25 and ~30‰, [40]. From Happo, 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.

Acknowledgment

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References
