Dear Dr. Kaiser,

With this letter we would like to summarise the changes and updates to the manuscript we have introduced preparing the revised version of our paper. We have considered all comments and accepted all of the suggestions proposed by the Referees, except a few instances that either were unclear to us or arouse from what we believe was a misunderstanding by the Referee #1 (please see the Author Comment submitted earlier for detailed answers).

The structure of the manuscript underwent minor modifications. We introduced subsections in Sect. 2 and relocated the information to amend the content flow, i.e. the on-line and WAS instrumentation setup, followed by the description of the results. Some discussion was moved from Sect. 2 to Sect. 3.

The content of the manuscript was amended substantially in Introduction (this section is almost rewritten), whilst minor improvements were introduced in Sects. 2.3, 3, 3.2. Two more references were added (Savarino and Morin, Stevens et al.). Furthermore, Fig. 1 was extended and Fig. 2 was corrected due to the error in our plotting software. We have added the Supplementary Material to the manuscript which includes four more figures requested by the Referees. Please see all changes between the manuscripts submitted to ACPD and ACP marked up in the following pages. Please note that we would like to leave the decision on some technical issues (e.g., use of the double superscript plus subscript notation) at your discretion.

Finally, our final Author Comment (AC C7938, pp. C7938–C7956) enumerates all referee comments and suggestions and the measures we have taken to address them. We appreciate very much the time you spent for editing this paper.

With best regards,

Sergey Gromov
An estimation of the $^{18}\text{O}/^{16}\text{O}$ ratio of UT/LMS ozone based on artefact CO in air sampled during CARIBIC flights

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Abstract

An issue of $\text{O}_3$-driven artefact production of CO in the UT/LMS air analysed in the CARIBIC−1 project is being discussed. By confronting the CO mixing/isotope ratios obtained from different analytical instrumentation, we (i) Reject natural/artificial sampling and mixing effects as possible culprits of the problem, (ii) Ascertain the photochemical nature and quantify the strength of the effect in a general contamination kinetic framework, and (iii) Demonstrate the successful application of the isotope mass-balance calculations for inferring the isotope signature of the contamination source. The $^{18}\text{O}/^{16}\text{O}$ ratios of the latter unambiguously indicate the oxygen being inherited from $\text{O}_3$. The $^{13}\text{C}/^{12}\text{C}$ ratios hint at reactions of trace amounts of organics with ample stratospheric $\text{O}_3$ that could have yielded the artificial CO. While the exact contamination mechanism is not known, it is clear that the issue pertains only to the earlier (first) phase of the CARIBIC project. Finally, estimated UT/LMS ozone $^{18}\text{O}/^{16}\text{O}$ ratios are lower than those observed in the LMS within the same temperature range, suggesting that higher pressures (240−270 hPa) imply lower isotope fractionation controlling the local $\delta^{18}\text{O}(\text{O}_3)$ value.

1 Introduction

[1] Successful determination of the atmospheric carbon monoxide (CO) content based on the collection of air samples depends on the preservation of the mixing ratio of CO inside the
receptacle, from the point of sampling to the moment of physiochemical analysis in a laboratory. A well known example in our field of research is the filling of pairs of glass flasks at South Pole Station for analysis at NOAA in Boulder, Colorado, USA (Novelli et al., 1998). There, the duplicate air sampling allowed for a degree of quality control which in view of the long transit times, especially during polar winter, was a perhaps not perfect, but certainly a practical measure. Here we deal with a different case: Using aircraft-based collection of very large air samples rendered duplicate sampling unpractical, yet analyses could be performed soon after the sampling had taken place because of the proximity of the aircraft’s landing location to the laboratory involved. A presumption of the analytical integrity of the process was that the growth of CO in receptacles is gradual and takes its time. Reminding Thomas Henry Huxley’s statement, “The great tragedy of Science – the slaying of a beautiful hypothesis by an ugly fact”, it turned out, however, that for air collected in stainless steel tanks in the upper troposphere/lowermost stratosphere (UT/LMS) higher CO values were measured in the laboratory than measured in situ during the collection of these air samples. Moreover, measurement of the stable oxygen isotopic composition of CO from these tanks revealed additional isotopic enrichments in $^{18}$O of 10‰ or more. It was soon realised that this phenomenon was due to the formation of CO in these tanks and/or possibly in the sampling system and inlet tubing used, by reactions involving ozone (Brenninkmeijer et al., 1999).

[2] Unexpectedly high $^{18}$O/$^{16}$O ratios in stratospheric ozone ($O_3$) were discovered by Konrad Mauersberger using a balloon-borne mass spectrometer (Mauersberger, 1981), which has triggered a series of theoretical and experimental studies on atmospheric $O_3$ heavy isotope enrichments (see, e.g., Schinke et al. (2006) for a review). In view of the advances in theoretical and laboratory studies on the isotopic composition of $O_3$, atmospheric measurements are welcome, they do however form a challenge. In the stratosphere $O_3$ is abundant, but the remoteness of the sampling domain is a problem. In the troposphere, low $O_3$ concentrations are the main obstacle, as indicated by few experiments performed to date (Krankowsky et al., 1995; Johnston and Thiemens, 1997; Vicars and Savarin, 2014). Nevertheless, recent analytical improvements, namely the use of an indirect method of reacting atmospheric $O_3$ with a substrate that can be analysed for the isotopic composition of the $O_3$-derived oxygen (Vicars et al., 2012), has greatly improved our ability to obtain information on the $O_3$ isotopic composition.

[3] Although the increase of CO concentrations in air stored in vessels is a well recognised problem, to our knowledge a specific $O_3$-related process has not been reported yet. Here we...
discuss this phenomenon and turn its disadvantage into an advantage, namely that of obtaining a valid estimate of the oxygen isotopic composition of $\text{O}_3$ in the UT/LMS, an atmospheric domain not yet covered by specific measurements. The air samples we examine in this study were collected onboard a passenger aircraft carrying an airfreight container with analytical and air/aerosol sampling equipment on long distance flights from Germany to South India and the Caribbean within the framework of the CARIBIC project (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container, http://www.caribic-atmospheric.com).

2 Experimental and results

2.1 Whole air sampling

[4] CARIBIC−1 (Phase #1, abbreviated hereafter “C1”) was operational from November 1998 until April 2002 using a Boeing 767-300 ER operated by LTU International Airlines (Brenninkmeijer et al., 1999). Using a whole air sample (WAS) collection system, twelve air samples were collected per flight (of ~10 hours duration at cruise altitudes of 10−12 km) in stainless steel tanks for subsequent laboratory analysis of the abundances of various trace gases, including $^{14}$CO. Large air samples were required in view of the ultra-low abundance of this mainly cosmogenic tracer (10−100 molecules cm$^{-3}$ STP, about 40−400 amol/mol). Each C1 WAS sample (holding ~350 litres of air STP) was collected within 15−20 min intervals representing the integral of the compositions encountered along flight segments of ~250 km. The overall uncertainty of the measured WAS [CO] is less than ±1% for the mixing ratio and ±0.1‰/±0.2‰ for $\delta^{13}$C(CO)/$\delta^{18}$O(CO), respectively (Brenninkmeijer, 1993; Brenninkmeijer et al., 2001). Isotope compositions are reported throughout this manuscript using $\delta^i = (R^i/R_{\text{std}}−1) \times 10^{−6}$ relating the ratio of rare over abundant isotopes $R^i$ of interest ($i$ denotes $^{13}$C, $^{16}$O or $^{17}$O) to the standard ratio $R_{\text{std}}$. These are V-SMOW of 2005.20×10$^{−6}$ for $^{18}$O/$^{16}$O (Gonfiantini, 1978; Coplen, 1994) and 386.72×10$^{−6}$ for $^{17}$O/$^{16}$O (Assonov and Brenninkmeijer, 2003), and V-PDB of 11237.2×10$^{−6}$ for $^{13}$C/$^{12}$C (Craig, 1957), respectively. As we mention above, the oxygen isotopic composition of the CO present in these WAS samples was corrupted, in particular when $\text{O}_3$ levels were as high as 100−600 nmol/mol.

[5] CARIBIC−2 (Phase #2, referred to as “C2”) started operation in December 2004 with a Lufthansa Airbus A340-600 fitted with a new inlet system and air sampling lines, including
PFA lined tubing for trace gas intake (Breninkmeijer et al., 2007). No flask CO mixing/isotope ratio measurements are performed in C2.

2.2 On-line instrumentation

In addition to the WAS collection systems, both C1 and C2 measurement setups include different instrumentation for on-line detection of [CO] and [O_3] (hereinafter the squared brackets [] denote the abundance, i.e. concentration or mixing ratio, of the respective species). In situ CO analysis in C1 is done using a gas chromatography (GC)-reducing gas analyser which provides measurements each 130 s with uncertainty of ±3 nmol/mol (Zahn et al., 2000). In C2, a vacuum ultraviolet fluorescence (VUV) instrument with lower measurement uncertainty and higher temporal resolution of ±2 nmol/mol in ~2 s (Scharffe et al., 2012) is employed, respectively. Furthermore, the detection frequency for O_3 mixing ratios has also increased, viz. from 0.06 Hz in C1 to 5 Hz in C2 (Zahn et al., 2002; Zahn et al., 2012).

2.3 Results

When comparing the CO abundances in relation to O_3 mixing ratios for C1 and C2, differences are apparent in the LMS, where C2 CO values are systematically lower. This is illustrated in Figure 1 (a) which presents the LMS CO-O_3 distribution of the C2 measurements overlaid with the C1 in situ and WAS data. For the in situ CO datasets we calculated the statistics (ibid., Panel (b)) of the samples with respective O_3 abundances clustered in 20 nmol/mol bins, i.e. the median and spread of [CO] as a function of [O_3] analysed. (The interquartile range, IQR, is used in the current analysis as a robust measure of the data spread instead of the standard deviation.) The data exhibit large [CO] variations at [O_3] below 400 nmol/mol that primarily reflect pronounced seasonal variations in the NH tropospheric CO abundance. With O_3 rising, [CO] increasingly becomes stratospheric, and its spread reduces to mere 3.5 nmol/mol and less, as [O_3] surpasses 500 nmol/mol. Despite the comparable spread in C1 and C2 [CO], from 400 nmol/mol of [O_3] onwards the C1 CO mixing ratios start to level off, with no samples below 35 nmol/mol having been detected, whereas the C2 levels continuously decline. By the 580 nmol/mol O_3 bin, C1 [CO] of 39.7±3.7 nmol/mol accommodates some extra 15 nmol/mol compared to 25.6±1.7 nmol/mol typical for C2 values. Overall, at [O_3] above 400 nmol/mol the conspicuously high [CO] is marked in about 200 in situ C1 samples, of which 158 and 69 emerge as statistically significant mild and extreme outliers, respectively, when compared against the ample (n~3·10^5) C2 statistics. (The conventions here follow...
Natrella (2003), i.e. ±1.5 and ±3 IQR ranges define the inner and outer statistical fences (ranges outside which the data points are considered mild and extreme outliers) of the C2 [CO] distribution in every \( O_3 \) bin, respectively; the statistics include the samples in bins with average \([O_3]\) of 420–620 nmol/mol. None of C1 CO at \([O_3]\) above 560 nmol/mol agrees with the C2 observations. Because the CO levels cannot have changed over the period in question by the difference we find (up to 55%), artefacts and calibration issues need to be scrutinised.

Unnatural elevations in the \( ^{18}O/^{16}O \) ratios of CO from WAS measurements are also evident, as shown in Fig. 2. The large \( \delta^{18}O(CO) \) departures that reach beyond +16‰ are found to be proportional to the concomitant \( O_3 \) abundances (denoted with colour) and more prominent at lower \([CO]\) (see also Fig. S2 in the Supplementary Material). A rather different relationship, however, is expected from our knowledge of UT/LMS CO sources (plus their isotope signatures) and available in situ observations (ibid., shown with triangles), as elucidated by Brenninkmeijer et al. (1996) (hereafter denoted as “B96”). That is, the more stratospheric CO is, the greater fraction of its local inventory is refilled with the photochemical component stemming from methane oxidation with a characteristic \( \delta^{18}O \) signature of ~0‰ or lower (Brenninkmeijer and Röckmann, 1997). This occurs because the CO sink at ruling UT/LMS temperatures proceeds more readily than its production, as the reaction of hydroxyl radical (OH) with CO, being primarily pressure-dependent, outcompetes the temperature-sensitive reaction of OH with CH\(_4\). Furthermore, as the lifetime of CO quickly decreases with altitude, transport-mixing effects take the lead in determining the vertical distributions of [CO] and \( \delta^{18}O(CO) \) above the tropopause, hence their mutual relationship. This is seen from the B96 data at \([CO]\) below 50 nmol/mol that line-up in a near linear relationship towards the end-members with lowest \( ^{18}O/^{16}O \) ratios. These result from the largest share of the \( ^{18}O \)-depleted photochemical component and extra depletion caused by the preferential removal of C\(^{18}O \) in reaction with OH (fractionation about -11‰ at pressures below 300 hPa, Stevens et al., 1980; Röckmann et al., 1998b).

It is beyond doubt that the enhancements of C1 C\(^{18}O \) originate from \( O_3 \), whose large enrichment in heavy oxygen (above +60‰ in \( \delta^{18}O \), Brenninkmeijer et al., 2003) is typical and found transferred to other atmospheric compounds (see Savarino and Morin (2012) for a review). In Fig. 2 it is also notable that not only the LMS compositions are affected, but elevations of (3–10)% from the bulk \( \delta^{18}O(CO) \) values are present in more tropospheric samples with [CO] of up to ~100 nmol/mol. These result from the dilution of the least affected tropospheric air with high mixing ratios by CO-poor, however substantially contaminated,
stratospheric air, sampled into the same WAS tank. Such sampling-induced mixing renders an
unambiguous determination of the artefact source’ isotope signature rather difficult, because
neither mixing nor isotope ratios of the admixed air portions are known sufficiently well (see
below).

Differences between the WAS and in situ measured [CO] – a possible indication that the
δ¹⁸O(CO) contamination pertains specifically to the WAS data – average at \( \Delta_{\text{WAS-in situ}} = 5.3\pm0.2 \) nmol/mol (1 SD of the mean, \( n = 408 \)) and happen to be random with respect to any
operational parameter or measured characteristic in C1, i.e. irrespective of CO or O₃
abundances. The quoted mixing ratio discrepancy remained after several calibrations between
the two systems had been performed, and likely results from the differences in the detection
methods, drifts of the calibration standards used (see details in Brenninkmeijer et al., 2001) and
a short-term production of CO in the stainless steel tanks during sampling. The large spread of
\( \Delta_{\text{WAS-in situ}} \) of ±3.5 nmol/mol (1σ of the population) ensues from the fact that the in situ
sampled air corresponds to (2−4)% of the concomitantly sampled WAS volume, as typically
6−7 in situ collections of ~5 s were made throughout one tank collection of 17−21 min. The
integrity of the WAS CO is further affirmed by the unsystematic distribution of the artefact
compositions among tanks (an opposite case for δ¹⁸O(CO₂) in C1 is discussed by
Assonov et al., 2009). Overall, the WAS and in situ measured CO mixing ratios correlate
extremely well (adj. \( R^2 = 0.972 \), slope of 0.992±0.008 (1σ), \( n = 408 \)). However, both anomalies
in [CO] and δ¹⁸O(CO) manifest clear but complex functions of the concomitant [O₃]. That is,
the C1 in situ and WAS data very likely evidence artefacts pertaining to the \( O_3 \)-driven effect of
the same nature. Below we ascertain and quantify these.

3 Discussion

Three factors may lead to the (artefact) distributions such as seen for C1 in situ [CO] at the
LMS \( O_3 \) abundances, namely:

(i) Strong (linear) natural mixing, such as enhanced stratosphere-troposphere exchange
(STE), when a [CO] outside the statistically expected range results from the integration of air
having dissimilar ratios of the tracers’ abundances, viz. \( \rho_{O_3:CO} = [O_3]/[CO] \). For example, mixing
of two air parcels in a 15%:85% proportion (by moles of air) with typical \( \rho_{O_3:CO} \) of 700:24
(stratospheric) and 60:125 (tropospheric), respectively, yields an integrated composition with
\( \rho_{O_3:CO} \) of ~580:40 which indeed corresponds to C1 data (this case is exemplified by the mixing
curve in Fig. 1). Nonetheless, occurrences of rather high (compared to the typical 24–26 nmol/mol) stratospheric CO mixing ratios (in our case, ~40 nmol/mol at the concomitant [O3] of 500–600 nmol/mol) are rare. For instance, a deep STE similar to that described by Pan et al. (2004) was observed by C2 only once (cf. the outliers at [O3] of 500 nmol/mol in Fig. 1), whereas the C1 outliers were exclusively registered in some 12 flights during 1997–2001. No relation between these outliers and the large-scale [CO] perturbation due to extensive biomass burning in 1997/1998 (Novelli et al., 2003) is established, otherwise elevated CO mixing ratios should manifest themselves at lower [O3] as well. Other tracers detected in CARIBIC provide supporting evidence against such strongly STE-mixed air having been captured by C1. That is, the binned distributions for the water vapour and de-trended N2O (similar to that for [CO] vs. [O3] presented in Fig. 1, not shown here) are greatly similar in C1 and C2. Whereas the small relative variations in atmospheric [N2O] merely confirm matching [O3] statistics in CARIBIC, the stratospheric [H2O] distributions witness no \( \rho_{O3:H2O} \) values corresponding to the C1 outliers’ \( \rho_{O3:CO} \), suggesting the latter being unnaturally low.

[jj] Mixing effects can also occur artificially, originating from sampling peculiarities or data processing. Since the CARIBIC platform is not stationary, about 5 s long sampling of an \textit{in situ} air probe in C1 implies integration of the compositions encountered along some hundred metres, owing to the high aircraft speed. This distance may cover a transect between tropospheric and stratospheric filaments of much different compositions. The effect of such ‘translational mixing’ can be simulated by averaging the sampling data with higher temporal frequency over longer time intervals. In this respect, the substantially more frequent CO data in C2 (<1 s) were artificially averaged over a set of increasing intervals to reckon whether the long sampling period in C1 could be the culprit for skewing its CO–O3 distribution. As a result, the original C2 data and their averages (equivalent to the C1 CO sample injection time) differ negligibly, as do the respective \( \rho_{O3:CO} \) values; the actual C2 CO–O3 statistic in the region of interest ([O3] of 540–620 nmol/mol) remains insensitive to integration of up to 300 s. Furthermore, a very strong artificial mixing with an averaging interval of at least 1200 s (comparable to C1 WAS sampling time) is required to yield the averages from the C2 data with \( \rho_{O3:CO} \) characteristic for the C1 outliers.

[iii] In view of the above, it is unlikely that any natural or artificial mixing processes are involved in the stratospheric [CO] discrepancies seen in C1. It therefore stands to reason to conclude that the sample contamination in C1 occurred prior the probed air reaching the analytical/sampling instrumentation in the container, since clearly elevated stratospheric CO
mixing ratios are common to WAS and in situ data. Two more indications, viz. growing [CO] discrepancy with increasing O₃ abundance, and the strong concomitant signal in δ¹⁸O(CO), imply that O₃-mediated photochemical production of CO took place. Further, by confronting the C1 and C2 [CO] measurements in a kinetic framework (detailed in Appendix A), we quantify the artefact CO component being chiefly a function of O₃ abundance as

\[ C_c = b \cdot [O_3]^2, \quad b = (5.19 \pm 0.12) \cdot 10^{-5} \text{ [mol/nmol]}, \]

which is equivalent to 8–18 nmol/mol throughout the respective [O₃] range of 400–620 nmol/mol (see Fig. 1 (d)). Subtracting this artefact signal yields the corrected in situ C1 CO–O₃ distribution conform to that of C2 (cf. red symbols in Fig. 1 (a)).

Importantly, since we can quantify the contamination strength using only the O₃ abundance, the continuous in situ C1 [O₃] data allows to estimate the integral artefact CO component in each WAS sample and, if the isotope ratio of contaminating O₃ is known, to derive the initial δ¹⁸O(CO). The latter, as it was mentioned above, is subject to strong sample-mixing effects, which is witnessed by δ¹⁸O(CO) outliers even at relatively high [CO] up to 100 nmol/mol. Accounting for such cases is, however, problematic since it is necessary to distinguish the proportions of the least modified (tropospheric) and significantly affected (stratospheric) components in the resultant WAS sample mix. In reality, however, this information is not available, therefore we applied an ad hoc correction approach (which is capable of determining the contamination source (i.e., O₃) isotope signature as well), as described in the following.

### 3.1 Contamination isotope signatures

Practically we resort to the differential mixing model (MM, originally known as the “Keeling-plot”), because it requires only the estimate of the artefact component mixing ratio, but no assumptions on the (unknown) shares and isotope signatures of the air portions mixed in a given WAS tank. The MM parameterises the admixing of the portion of artefact CO to the WAS sample with the "true" initial composition, as formulated below:

\[
\begin{align*}
\delta_i' & = C_i' \delta_i + C_c' \delta_c \\
C_i & = (C_a - C_c)
\end{align*}
\]

where indices \(a\), \(c\) and \(t\) distinguish the abundances C and isotope compositions \(\delta\) (\(i\) may refer to \(^{13}\)C or \(^{18}\)O) pertaining to the analysed sample, estimated contamination and "true" composition sought (i.e., \(C_t\) and \(\delta_t\), respectively. (Here the contamination strength \(C_c\) is derived...
by integrating Eq. (1) using the in situ C1 [O3] data for each WAS sample. By rewriting the above equation w.r.t. the isotope signature of the admixed portion $\delta_i$, one obtains:

$$\delta_i = \delta_t + \left(\delta_a - \delta_t\right) \left(1 + C_i / C_t\right),$$

which signifies that linear regression of the measured $\delta_i$ as a function of the reciprocal of $C_t$ yields the estimated contamination signature $\delta_c$ at $(C_t)^{-1} \to 0$. (The Keeling plot detailing the calculations with the MM is shown in Supplementary Material, Fig. S3.) The MM described by Eq. (2) provides adequate results only for the invariable initial compositions $(C_t, \delta_t)$, therefore we apply it to the subsets of samples picked according to the same reckoned $C_t$ (within a ±2 nmol/mol window, $n > 7$). Such selection, however, may be insufficient: Due to the strong sampling effects in the WAS samples (see previous Section), it is possible to encounter samples that integrate different air masses to the same reckoned $C_t$ but rather different average $\delta_t$. The solution in this case is to refer to the goodness of the MM regression fit, because the $R^2$ intrinsically measures the linearity of the regressed data, i.e. closeness of the “true” values in a regarded subset of samples, irrespective of underlying reasons for that.

[17] Higher $R^2$ values thus imply higher consistency of the estimate, as demonstrated in Fig. 3 showing the calculated $\delta_i$ for $C_t$ below 80 nmol/mol as a function of the regression $R^2$. The latter decreases with greater $C_t$ (i.e., larger sample subset size, since tropospheric air is more often encountered) and, conformably, larger variations in $\delta_i$. Ultimately, at lower $R^2$ the inferred $^{18}$O signatures converge to values slightly above zero expected for uncorrelated data, i.e. C1 $^{18}$O(CO) tropospheric average. A similar relationship is seen for the $^{13}$C signatures (they converge around −28‰), however, there are no consistent estimates found ($R^2$ is generally below 0.4). Since such is not the case for $^{18}$O, the MM is not sufficiently sensitive to the changes caused by the contamination, which implies that the artefact CO $^{13}$C should be within the range of the “true” $^{13}$C(CO) values. Interestingly, the MM is rather responsive to the growing fraction of the CH4-derived component in CO with increasing [O3], as the $^{13}$C$\delta_i$ value of $(47.2\pm5.8)$‰ inferred at $R^2$ above 0.4 is characteristic for the $^{13}$C of methane in the UT/LMS. It is noteworthy that we have accounted for the biases in the analysed C1 WAS $^{13}$C(CO) expected from the mass-independent isotope composition of O3 (see details in Appendix B).

[18] We derive the “best-guess” estimate of the admixed CO $^{18}$O signature at $^{18}$O$\delta_i = +$(92.0±8.3)‰, which agrees with the other MM results obtained at $R^2$ above 0.75. Taking the same subsets of samples, the concomitant $^{13}$C signature matches $^{13}$C$\delta_i = -(23.3±8.6)$‰, indeed at the upper end of the expected LMS $^{13}$C(CO) variations of −(25–31)%o, which likely does
not allow the MM to ascertain this result as pertaining to the contamination (the corresponding 
$R^2$ values are below 0.1). Upon the correction using the inferred $^{18O}_{\delta_c}$ value, the C1 WAS 
$\delta^{18}$O(CO) data appear adequate (shown with red symbols in Fig. 2). That is, variations in the 
observed $^{18}$O are driven by (i) the seasonal/Regional changes in the composition of 
tropospheric air and by (ii) the degree of mixing or replacement of the latter with the 
stratospheric component that is less variable in $^{18}$O. This is seen as stretching of the scattered 
tropospheric values ([CO] above 60 nmol/mol) in a mixing fashion towards $\delta^{18}$O(CO) of around 
$-10\%$ at [CO] of about 25 nmol/mol, respectively. The corrected C1 $\delta^{13}$C(CO) data (shown in 
Supplementary Material, Fig. S4) are found to be in a $\pm1\%$ agreement with the observations by 
B96, except for several deep stratospheric samples ([CO] below 40 nmol/mol). The latter were 
encountered during "ozone hole" conditions and carried extremely low $^{13}$CO abundances, which 
was attributed to the reaction of methane with available free Cl radicals

(Brenninkmeijer et al., 1996).

3.2 Estimate of $\delta^{18}$O(O$_3$)

The $^{18O}_{\delta_c}$ signature inferred here ($^{18O}_{\delta_c} = + (92.0 \pm 8.3)\%$) unambiguously pertains to O$_3$ and is 
comparable to $\delta^{18}$O(O$_3$) values measured in the stratosphere at temperatures about 30K lower 
than those encountered in the UT/LMS by C1 (see Table 1 for comparison). If no other factors 
are involved (see below), this discrepancy in $\delta^{18}$O(O$_3$) should be attributed to the local 
conditions, i.e. the higher pressures (typically 240–270 hPa for C1 cruising altitudes) at which 
O$_3$ was formed. Indeed, the molecular lifetime (the period through which the species' isotope 
reservoir becomes entirely renewed, as opposed to the "bulk" lifetime) of O$_3$ encountered along 
the C1 flight routes is estimated on the order of minutes to hours at daylight (H. Riede, MPI-C, 
2010), thus the isotope composition of the photochemically regenerated O$_3$ resets quickly 
according to the local conditions. Virtual absence of sinks, in turn, leads to "freezing" of the 
$\delta^{18}$O(O$_3$) value during night in the UT/LMS. Verifying the current $\delta^{18}$O(O$_3$) estimate against the 
kinetic data, in contrast to the stratospheric cases, is problematic. The laboratory studies on O$_3$ 
formation to date have scrutinised the concomitant kinetic isotope effects (KIEs) as a function 
of temperature at only low pressures (50 Torr); the attenuation of the KIEs with increasing 
pressure was studied only at room temperatures (see Table 1, also Brenninkmeijer et al. (2003) 
for references). A rather crude attempt may be undertaken by conjecturing an inhibition of the 
formation KIEs proportional to that measured at $\sim$320K, however applied to the nominal low-
pressure values reckoned at (220–230)K. A decrease in $\delta^{18}$O(O$_3$) of about (5.9–7.6)\% is
expected from such calculation, yet accounting for a mere one-half of the (13.3−14.6)% “missing” in $^{18}$O.

[20] Lower $^{18}$O values could result from possible isotope fractionation accompanying the production of the artefact CO. Although not quantifiable here, oxygen KIEs in the $\text{O}_3 \rightarrow \text{CO}$ conversion chain cannot be ruled out, recalling that the intermediate reaction steps are not identifiable and the artefact CO represents at most 4% of all $\text{O}_3$ molecules. Furthermore, the yield $\lambda_{\text{O}_3}$ of CO from O$_3$ may be lower than unity (see details in Appendix A). On the other hand, the inference that the contamination strength primarily depends on $[\text{O}_3]$ indicates that the kinetic fractionation may have greater effect on the carbon isotope ratios of the artefact CO produced (the $^{13}$C$\delta_c$ values) in contrast to the oxygen ones. That is because all reactive oxygen available from $\text{O}_3$ becomes converted to CO, whilst the concomitant carbon atoms are drawn from a virtually unlimited pool whose apparent isotope composition is altered by the magnitude of the $^{13}$C KIEs.

[21] Besides KIEs, selectivity in the transfer of O atoms from $\text{O}_3$ to CO affects the resulting $^{18}$O$\delta_c$ value. The terminal O atoms in $\text{O}_3$ are enriched w.r.t. to the molecular (bulk) $\text{O}_3$ composition when the latter is above $\sim+70\%$ in $\delta^{18}$O (Janssen, 2005; Bhattacharya et al., 2008), therefore an incorporation of only central O atoms into the artefact CO molecules should result in a reduced apparent $^{18}$O$\delta_c$ value. Such exclusive selection is, however, less likely from the kinetic standpoint and was not observed in available laboratory studies (see Savarino et al. (2008) for a review). For instance, Röckmann et al. (1998a) established the evidence of direct O transfer from $\text{O}_3$ to the CO produced in alkene ozonolysis. A reanalysis of their results (in light of findings of Bhattacharya et al. (2008)) suggests that usually the terminal atoms of the $\text{O}_3$ molecule become transferred (their ratio over the central ones changes from the bulk $\sim2:1$ to $\sim1:0$ for various species). Considering the alternatives of the O transfer in our case (listed additionally in Table 1), the equiprobable incorporation of the terminal and central $\text{O}_3$ atoms into CO should result in the $\delta^{18}$(O$_3$) value in agreement with the “crude” estimate based on laboratory data given above.

[22] Furthermore, the conditions that supported the reaction of $\text{O}_3$ (or its derivatives) followed by the production of CO are vague. A few hypotheses ought to be scrutinised here. First, a fast $\text{O}_3 \rightarrow \text{CO}$ conversion must have occurred, owing to short (i.e., fraction of a second) exposure time of the probed air to the contamination. Accounting for the typical C1 air sampling conditions (these are: sampled air pressure of 240–270 hPa and temperature of 220–235K
outboard to 275−300K inboard, sampling rate of \( \sim 12.85 \cdot 10^{-3} \) moles s\(^{-1} \) corresponding to 350L STP sampled in 1200 s, inlet/tubing volume gauged to yield exposure times of 0.01 to 0.1 s due to variable air intake rate, \([\text{O}_3]\) of 600 nmol/mol, the overall reaction rate coefficient \((k_c\) in Eq. (A1) from Appendix A) must be on the order of \( 6 \cdot 10^{-15}/\tau_c \) [molec\(^{-1}\) cm\(^3\) s\(^{-1}\)], where \( \tau_c \) is the exposure time. Assuming the case of a gas-phase CO production from a recombinating \( \text{O}_3 \) derivative and an unknown carbonaceous compound \( \text{X} \), the reaction rate coefficient for the latter \((\tilde{k}_c\) in Eq. (A1) in Appendix A) must be rather high, at least \( \sim 6 \cdot 10^{-10} \) [molec\(^{-1}\) cm\(^3\) s\(^{-1}\)] over \( \tau_c = 1/100 \) s. This number decreases proportionally with growing \( \tau_c \) and [X], if we take less strict exposure conditions. Nonetheless, in order to provide the amounts of artefact CO we detect, a minimum abundance of 20 nmol/mol (or up to 4 µg of C per flight) of \( \text{X} \) is required, which is not available in the UT/LMS from the species readily undergoing ozonolysis, e.g., alkenes.

[23] Second, a more complex heterogeneous chemistry on the inner surface of the inlet or supplying tubing may be involved. Such can be the tracers’ surface adsorption, (catalytic) decomposition of \( \text{O}_3 \) and its reaction with organics or with surface carbon that also may lead to the production of CO (Oyama, 2000). Evidence exists for the dissociative adsorption of \( \text{O}_3 \) on the surfaces with subsequent production of the reactive atomic oxygen species (see, e.g., Li et al., 1998, also Oyama, 2000). It is probable that sufficient amounts of organics have remained on the walls of the sampling line exposed to highly polluted tropospheric air, to be later broken down by the products of the heterogeneous decomposition of the ample stratospheric \( \text{O}_3 \). Unfortunately, the scope for a detailed quantification of intricate surface effects in the C1 CO contamination problem is very limited.

4 Conclusions

[24] Recapitulating, the in situ measurements of CO and \( \text{O}_3 \) allowed us to unambiguously quantify the artefact CO production from \( \text{O}_3 \) likely in the sample line of the CARIBIC−1 instrumentation. Strong evidence to that is provided by the isotope CO measurements. We demonstrate the ability of the simple mixing model (“Keeling-plot” approach) to single out the contamination isotope signatures even in the case of a large sampling-induced mixing of the air with very different compositions. Obtained as a collateral result, the estimate of the \( \delta^{18} \text{O}(\text{O}_3) \) in the UT/LMS appears adequate, calling, however, for additional laboratory data (e.g., the
temperature-driven variations of the O$_3$ formation KIE at pressures above 100 hPa) for a more unambiguous verification.

Appendix A. Contamination kinetic framework

[25] We infer the O$_3$-exclusive functional dependence of the contamination strength C$_c$ by discriminating the C1 outliers from respective C2 data in the following kinetic framework:

\[
\begin{align*}
\text{O}_3 &\rightarrow \alpha_k \left(\left[\ldots + X \rightarrow \ldots \right] \rightarrow \lambda_{O_3} \text{CO} \right)
\end{align*}
\]

where \( k_c \) denotes the overall pseudo-first-order rate coefficient of the reaction chain leading to the artefact CO production with the respective yield \( \lambda_{O_3} \). The individual rate coefficients \( \alpha_k \) and \( \lambda_{O_3} \) pertain to the unknown compound(s) X and O$_3$ reacting with the integral stoichiometry factors \( K \) and \( \kappa \), respectively. Practically we find that variations in C$_c$ are exhaustively described using \([\text{O}_3]\), \( \kappa \) and \( k_c \) (the latter are obtained in a regression analysis). The value of \( k_c \) thus integrates the influence of the unknown (and likely invariable) \( [X] \), \( \lambda_{O_3} \) and \( K \). The relation defined by Eq. (A1) provides the best approximation for C$_c$ as a function of \([\text{O}_3]\) at \( \kappa = 2.06 \pm 0.38 \), suggesting two chain steps involving O$_3$ or its derivatives. At \( \kappa = 2 \), the ratio C$_c$/[O$_3$]$^2$ (essentially proportional to the reaction time \( \tau_c \) and overall rate coefficient \( k_c \)) is found to be \((5.19 \pm 0.12) \times 10^{-5} \text{ mol/nmol} (\pm 1\sigma, \text{adj. } R^2 = 0.83, \text{red. } \chi^2 = 4.0) \). The low uncertainty (within \( \pm 3\% \)) of this estimate signifies an exclusive dependence of the contamination source on the O$_3$ abundance, as well as much similar reaction times \( \tau_c \). It is possible to constrain the overall yield \( \lambda_{O_3} \) of CO molecules in the artefact source chain to be between 0.5 and 1, comparing the magnitude of C$_c$ to the discrepancy between the \([\text{O}_3]\) measured in C1 and C2 (\( \pm 20 \text{ nmol/mol} \), taken equal to the \([\text{O}_3]\) bin size owing to the N$_2$O–O$_3$ and H$_2$O–O$_3$ distributions matching well between the datasets). Lower \( \lambda_{O_3} \) values, otherwise, should have resulted in a noticeable (\( i.e. \), greater than 20 nmol/mol) decrease in the C1 O$_3$ abundances with respect to the C2 levels.
Appendix B. Corrections to measured $\delta^{13}$C(CO) values due to the oxygen MIF

Atmospheric O$_3$ carries an anomalous isotope composition (or mass-independent fractionation, MIF) with a substantially higher relative enrichment in $^{17}$O over that in $^{18}$O (above +25‰ in $\Delta^{17}$O = (δ$^{17}$O+1)/(δ$^{18}$O+1)$^{\beta}$−1, $\beta = 0.528$) when compared to the majority of terrestrial oxygen reservoirs that are mass-dependently fractionated (i.e., with $\Delta^{17}$O of ~0‰) (see Brenninkmeijer et al. (2003) and refs. therein). CO itself also has an unusual oxygen isotopic composition, possessing a moderate tropospheric MIF of around +5‰ in $\Delta^{17}$O(CO) induced by the sink KIEs in reaction of CO with OH (Röckmann et al., 1998b; Röckmann et al., 2002) and a minor source effect from the ozonolysis of alkenes (Röckmann et al., 1998a; Gromov et al., 2010). A substantial contamination of CO by O$_3$ oxygen induces proportional changes to $\Delta^{17}$O(CO) that largely exceed its natural atmospheric variation. Furthermore, the MIF has implications in the analytical determination of $\delta^{13}$C(CO), because the presence of C$^{17}$O species interferes with the mass-spectrometric measurement of the abundances of $^{13}$CO possessing the same basic molecular mass ($m/e$ is 45). When inferring the exact C$^{17}$O/C$^{18}$O ratio in the analysed sample is not possible, analytical techniques usually involve assumptions (e.g., mass-dependently fractionated compositions or a certain non-zero $\Delta^{17}$O value) with respect to the C$^{17}$O abundances (Assonov and Brenninkmeijer, 2001). In effect for the C1 CO data, the artefact CO produced from O$_3$ had contributed with unexpectedly high C$^{17}$O abundances that led to the overestimated $\delta^{13}$C(CO) analysed. Knowing the contamination magnitude C$_c$ and assuming the typical O$_3$ MIF composition being $^{17}$Δ$\alpha$, the respective bias $^{13}$C$\delta_b$ is calculated using

$$\Delta^{17}$O(CO) $\approx \left[ \frac{^{17}$\Delta$\alpha C_c + ^{13}$\Delta$\alpha C_s}{C_s} \right] (C_s)^{-1},$$  
\text{(B1)}

where $^{17}$Δ$\alpha$ denotes the natural, i.e. expected “true” value of $\Delta^{17}$O(CO). The remaining parameters pertain to the contamination kinetic framework (see Appendix A, Eq. (A1)). For the purpose of the current estimate it is sufficient to take $^{17}$Δ$\alpha$ of +5‰ representing equilibrium enrichments expected in the remote free troposphere and UT/LMS. For the O$_3$ MIF signature $^{17}$Δ$\alpha$, the value of +30‰ (the average $\Delta^{17}$O(O$_3$) expected from the kinetic laboratory data at conditions met along the C1 flight routes, see Sect. 3.2 and Table 1) is adopted. The coefficient that proportionates $^{13}$C$\delta_b$ and $\Delta^{17}$O in Eq. (B1) is reckoned for the CO with initially unaccounted...
MIF (e.g., the sample is assumed to be mass-dependently fractionated) and quantifies some
extra +0.73‰ in the analysed δ^{13}C(CO) per every +10‰ of Δ^{17}O(CO) excess (Assonov and
Brenninkmeijer, 2001). The most contaminated C1 WAS CO samples at [O_3] above
300 nmol/mol are estimated to bear Δ^{17}O(CO) of (6–12)% corresponding to fractions of
(0.10–0.27) of the artefact CO in the sample. Accordingly, the reckoned δ^{13}C(CO) biases span
(0.5–0.9)‰. Although not large, these will exceed the δ^{13}C(CO) measurement precision of
±0.1‰ and were corrected for, and therefore are taken into account in the calculations with the
MM presented in Sect. 3.1.

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Table 1. Ozone $^{18}$O/$^{16}$O isotope ratios from literature and this study

<table>
<thead>
<tr>
<th>Domain</th>
<th>T [K]</th>
<th>P [hPa]</th>
<th>δ$^{18}$O(O$_3$) [%]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stratosphere</td>
<td>190−210</td>
<td>13−50</td>
<td>83−93 (&lt;3)</td>
<td></td>
</tr>
<tr>
<td>UT/LMS</td>
<td>220−235</td>
<td>240−270</td>
<td>89−95 (8)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>84−88 (6) T</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>91−98 (9) TC</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>112−124 (17) C</td>
<td></td>
</tr>
<tr>
<td>Laboratory</td>
<td>190−210</td>
<td>~67</td>
<td>87−97 (6)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>220−235</td>
<td>~67</td>
<td>102−110 (6)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>220−235</td>
<td>240−270</td>
<td>95−103</td>
<td></td>
</tr>
</tbody>
</table>

Notes: Values in parentheses denote the average of the estimates’ standard errors. The expected O$_3$ isotope composition on the V-SMOW scale is calculated from the O$_3$ enrichments ε reported relative to O$_2$ using

$$δ^{18}O(O_3)_{V\text{-SMOW}} = δ^{18}O(O_2)_{V\text{-SMOW}} + ε^{18}O(O_3)/ε^{18}O(O_2).$$

1) Observations (see Krankowsky et al. (2007) and refs. therein), lowermost values (19−25 km). Quoted temperature range is derived by matching measured δ$^{18}$O(O$_3$) and laboratory data (see note 2).
2) This study, C1 observations (10−12 km). Letters denote the estimates derived using the data from Bhattacharya et al. (2008) and assuming only terminal (T), only central (C) and equiprobable terminal and central (TC) O$_3$ atoms transfer to the artefact CO.
3) Calculated using the laboratory KIE temperature dependence data summarised by Janssen et al. (2003).
4) Calculated assuming a pressure dependence of the O$_3$ formation KIE similar to that measured at 320K (see Guenther et al. (1999) and refs. therein).
Figure Captions

Fig. 1. (a) Distribution of CO mixing ratios as a function of concomitant O_3 mixing ratios measured by CARIBIC in the LMS ([O_3]>300 nmol/mol). The shaded area is the two-dimensional histogram of the C2 measurements (all C2 data obtained until June 2013) counted in 5×1 nmol/mol size [O_3]×[CO] bins, thus darker areas emphasise greater numbers of particular CO–O_3 pairs observed. Small symbols denote the original C1 \textit{in situ} measurements (black) and corrected for the artefacts (red); the C1 WAS analyses (11 of total 408) are shown with large symbols. Thin and thick step-lines demark the inner and outer statistical fences (ranges outside which the data points are considered mild or extreme outliers, see text) of the C2 data, respectively. The dashed curve exemplifies compositions expected from the linear mixing of very different (e.g., tropospheric and stratospheric) end-members. (b) Statistics on CO mixing ratios from C1 and C2 data shown in box-and-whisker diagrams for samples clustered in 20 nmol/mol O_3 bins (whiskers represent 9th/91st percentiles). (c) Sample statistic for each CARIBIC dataset (note the C2 figures scaled down by a factor of 1000). (d) Estimates of the C1 \textit{in situ} CO contamination strength C_c as a function of [O_3] (solid line) obtained by fitting the difference ΔCO between the C2 and C1 \textit{in situ} [CO] (small symbols) in the kinetic framework (see Appendix A, Eq. (A1)). Step line shows the ΔCO for the statistical averages (the shaded area equals the height of the inner statistical fences of the C2 data). Large symbols denote the estimates of C_c in the C1 WAS data (slight variations vs. \textit{in situ} data are due to the sample mixing effects, see Sect. 3). Colour denotes the respective C1 WAS δ_{18}O(CO) (note that typically 6–7 \textit{in situ} measurements correspond to one WAS sample). Note: The entire C1 CO/O_3 dataset is presented in the Supplementary Material, Fig. S1.

Fig. 2. \textsuperscript{18}O/\textsuperscript{16}O isotope composition of CO as a function of its reciprocal mixing ratio. Triangles present the data from the remote SH UT/LMS obtained by Brenninkmeijer \textit{et al.} (1996) (B96). Colour refers to the concomitantly observed O_3 abundances; note the extremely low [O_3] encountered by B96 in the Antarctic "ozone hole" conditions. Filled and hollow circles denote the original and corrected (as exemplified by the dashed arrow) C1 WAS data, respectively, with the symbol size scaling proportional to the estimated contamination magnitude (see text).

Fig. 3. Results of the regression calculation with the MM. Shown with symbols are the source isotope signatures \(\delta_i\), as a function of the respective coefficient of determination (\(R^2\)). Colour denotes the number of samples in each subset selected. Solid and dashed lines present the best guess \(\pm 1\) SD for the \(\delta_{18}O(O_3)\) and \(3^{13}C(C_c)\) estimates. Dashed circles mark the values obtained at highest \(R^2\) for \(\delta_{18}O(O_3)\) regression (above 0.9). See text for details.
greater. It was soon realised that this phenomenon was due to the formation of CO in these tanks and/or in the sampling system and inlet tubing used, by reactions involving ozone (Brenninkmeijer et al., 1999).

Unexpectedly high $^{18}$O/$^{16}$O ratios in stratospheric ozone ($O_3$) were discovered by Konrad Mauersberger using a balloon-borne mass spectrometer (Mauersberger, 1981).

However, measurement of the atypical $^{18}$O and the subsequently discovered concomitant disproportionately high $^{17}$O enrichments of stratospheric $O_3$ were subject to its concentrations may be higher helps a good deal to obtain information on the $O_3$ isotopic composition.

The air samples we refer to here were collected onboard a passenger aircraft carrying an airfreight container with analytical and air/aerosol sampling equipment on long distance passenger flights between Germany and South India/the Caribbean within the framework of the CARIBIC project (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container, http://www.caribic-atmospheric.com).

C1 WAS samples for the laboratory analyses were collected in stainless steel tanks (holding ~350 litres of air STP) sampled within ~20 min intervals representing the integral of the compositions encountered along flight segments of ~250 km. The overall uncertainty of the measured WAS [CO] is less than ±1% for the mixing ratio and ±0.1‰/±0.2‰ for $\delta^{13}$C(CO)/$\delta^{18}$O(CO), respectively (Brenninkmeijer, 1993; Brenninkmeijer et al., 2001). The isotope compositions are reported throughout this manuscript using $\delta^{i} = (R_{i}/R_{st}-1)$ relating the ratio of rare over abundant isotopes $R$ of interest ($i$ denotes $^{13}$C, $^{18}$O or $^{17}$O) to the standard ratio $R_{st}$. These are V-SMOW of 2005.20×10^{-6} for $^{18}$O/$^{16}$O (Gonfiantini, 1978; Coplen, 1994) and 386.72×10^{-6} for $^{17}$O/$^{16}$O (Assonov and Brenninkmeijer, 2003), and V-PDB of 11237.2×10^{-6} for $^{13}$C/$^{12}$C (Craig, 1957), respectively.
(a) Distribution of CO mixing ratios as a function of concomitant O₃ mixing ratios measured by CARIBIC in the LMS ([O₃] > 300 nmol/mol). The shaded area is the two-dimensional histogram of the C2 measurements (all C2 data obtained until June 2013) counted in 5×1 nmol/mol size [O₃]×[CO] bins, thus darker areas emphasise greater numbers of particular CO–O₃ pairs observed. Small symbols denote the original C1 in situ measurements (black) and corrected for the artefacts (red); the C1 WAS analyses (11 of total 408) are shown with large symbols. Thin and thick step-lines demark the inner and outer statistical fences (ranges outside which the data points are considered mild or extreme outliers, see text) of the C2 data, respectively. The dashed curve exemplifies compositions expected from the linear mixing of very different (e.g., tropospheric and stratospheric) end-members.

(b) Statistics on CO mixing ratios from C1 and C2 data shown in box-and-whisker diagrams for samples clustered in 20 nmol/mol O₃ bins (whiskers represent 9th/91st percentiles). (c) Sample statistic for each CARIBIC dataset (note the C2 figures scaled down by a factor of 1000). (d) Estimates of the C1 in situ CO contamination strength Cₖ as a function of [O₃] (solid line) obtained by fitting the difference ΔCO between the C2 and C1 in situ [CO] (small symbols) in the kinetic framework (see Appendix A, Eq. (A1)). Step line shows the ΔCO for the statistical averages (the shaded area equals the height of the inner statistical fences of the C2 data). Large symbols denote the estimates of Cₖ in the C1 WAS data (slight variations vs. the in situ data are due to the sample mixing effects, see Sect. 3). Colour denotes the respective C1 WAS δ¹⁸O(CO) (note that typically 6–7 in situ measurements correspond to one WAS sample). Note: The entire C1 CO/O₃ dataset is presented in the Supplementary Material, Fig. S1.
Updated Fig. 2

Fig. 2. $^{18}$O/$^{16}$O isotope composition of CO as a function of its reciprocal mixing ratio. Triangles present the data from the remote SH UT/LMS obtained by Breninkmeijer et al. (1996) (B96). Colour refers to the concomitantly observed O$_3$ abundances; note the extremely low [O$_3$] encountered by B96 in the Antarctic "ozone hole" conditions. Filled and hollow circles denote the original and corrected (as exemplified by the dashed arrow) C1 WAS data, respectively, with the symbol size scaling proportional to the estimated contamination magnitude (see text).