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CO$_2$ isotope analyses using large air samples collected on intercontinental flights by the CARIBIC Boeing 767

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Analytical details for ^{13}C and ^{18}O isotope analyses of atmospheric CO$_2$ in large air samples are given. The large air samples of nominally 300 L were collected during the passenger aircraft-based atmospheric chemistry research project CARIBIC and analyzed for a large number of trace gases and isotopic composition. In the laboratory, an ultra-pure and high efficiency extraction system and high-quality isotope ratio mass spectrometry were used. Because direct comparison with other laboratories was practically impossible, the extraction and measurement procedures were tested in considerable detail. Extracted CO$_2$ was measured twice vs. two different working reference CO$_2$ gases of different isotopic composition. The two data sets agree well and their distributions can be used to evaluate analytical errors due to isotope measurement, ion corrections, internal calibration consistency, etc. The calibration itself is based on NBS-19 and also verified using isotope analyses on pure CO$_2$ gases (NIST Reference Materials (RMs) and NARCIS CO$_2$ gases). The major problem encountered could be attributed to CO$_2$-water exchange in the air sampling cylinders. This exchange decreased over the years. To exclude artefacts due to such isotopic exchange, the data were filtered to reject negative δ^{18}O(CO$_2$) values. Examples of the results are given. Copyright © 2009 John Wiley & Sons, Ltd.

National (e.g. NOAA-ESRL[1]) and international (WMO-GAW[2]) programs address a better understanding of the budget of atmospheric CO$_2$, the gas innate to life and climate on the planet. The CO$_2$ cycle and its budget are extremely complex and variable which renders atmospheric concentration measurements over a range of geographical scales from local to global necessary. Most frequently, boundary layer air is assayed, directly influenced by CO$_2$ sources and sinks, whereas several observatories reach into the free troposphere using mountain locations. Basically, global networks do cover remote areas (particularly the tropics) only sparsely. Likewise much less information is available at altitude, although satellite measurements are filling gaps in observation (e.g.[3–5]). To provide detailed information about CO$_2$ in background air, in the free tropical troposphere and in the tropopause region, far from CO$_2$ sources and sinks, aircraft observations are essential. Ideal in this respect is the use of civil aircraft, which in practice amounts to the use of passenger aircraft.[6] Two operational passenger aircraft based projects that measure CO$_2$ are the Japanese project CONTRAIL (Comprehensive Observatory Network for Trace Gases by Airliners)[7] and the European project CARIBIC (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container). The

project CARIBIC using a Boeing 767 (CARIBIC I) as discussed in this paper operated from 1997 until 2002, and resumed in 2005 using a Lufthansa Airbus A340-600.[8] CARIBIC is based on the monthly deployment of a large instrument container in the aircraft. The container is a flying automated analytical laboratory that also collects air and aerosol samples.

With the ultimate goal of improving estimates of sources, sinks and fluxes, CO$_2$ concentration is best measured in real time in a continuous mode. In doing so, episodes of pollution, local influences and background air can be identified. On a fast moving aircraft, the resolution attainable gives useful information about differences between air masses. Cross-sections of pollution plumes can be constructed. However, the NOAA-ESRL, CARIBIC I and the Japanese greenhouse gas project were all three originally based on flask sampling only. The temporal resolution is low; for instance, for samples from the NOAA-ESRL network weekly to biweekly. Nevertheless, an overpowering argument for using flask sampling is its inherent reliability resulting from a simple, effective approach with possibly one analytical system for all samples.

In addition to the practicality of laboratory analyses on air samples collected, an additional advantage is that a wide spectrum of analyses can be performed on the same sample. Of special relevance to CO$_2$ is its isotopic composition. Air samples allow highly accurate and precise measurements of isotopic compositions to be made.

The CARIBIC I instrument container[9] included instruments for real-time analyses of chiefly O$_3$, CO and aerosol.

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For air sampling an unusual air sample collector was used. This system could collect 12 large air samples in ~20 L volume stainless steel (SS) cylinders at a pressure of ~17 bar. The samples collected were analyzed for CO_2, CH_4, N_2O, SF_6, NMCHs (non-methane hydrocarbons), halogenated organic compounds as well as for CO, and its isotopologues ^{13}CO, $C^{18}O$ and ^{14}CO. The large sample volume was required to detect the ultra-low concentration (mainly cosmogenic) trace gas ^{14}CO (mixing ratio only 10^{-19} to 10^{-18}). In the process of extracting CO from large air samples first of all the air-CO_2 needs to be removed with very high efficiency. We also routinely retrieved this CO_2 which was subjected to accurate stable isotope analysis. From 2001 onwards careful corrections for instrumental effects were applied. Originally, however, CO_2 was a by-product of a study that targeted ^{14}CO as a cosmogenic tracer.

By virtue of the very large amount of CO_2 extracted (nominally 100 cm³ STP) using highly efficient Russian Doll traps,[10,11] the results obtained are of good quality. In this paper we render a detailed account of the isotope analyses and the corrections used. This information is of significance for the extraction and analyses of large amounts of CO_2 from air and leads to a better understanding of the corrections procedures. Although the technique is in contrast to the modern trend to perform analysis on small samples, and to develop on-line technologies, it is valuable to consider it as an independent system used for analyses of air masses from the free troposphere. The air extracts (~100 mL of CO_2 from ~300 samples) have been stored at Max Planck Institute for Chemistry (MPI-Chemistry) and some of these can be made available for use by other laboratories although, as we will show, comparisons are not trivial. The method (using large archived samples) also may be useful for 'clumped' isotope analyses,[12] in which masses 44, 45, 46 and 47 are analyzed, for which larger amounts of CO_2 are an advantage. For the current phase of the aircraft project, CARIBIC II, an air sampling system with 28 glass flasks, has been used since 2005. Isotope analyses of these samples started in 2007 using a dedicated isotope analysis system at Institute for Reference Materials and Measurements (IRMM) in Geel, Belgium. This method will be published separately.

EXPERIMENTAL

Air collection

The CARIBIC system and instrument container have been described previously.[9] The container was located in the forward cargo bay of a Boeing 767 (LTU International Airways) and connected to the dedicated air inlet underneath. A considerable part of the container was occupied by the large air sampler. Air samples were taken at cruising altitudes of 9–11 km by pressurizing air (ambient pressure about 200–250 hPa) by means of two diaphragm pumps (Vacuubrand, Wertheim, Germany) with four heads in parallel followed by a membrane pump (KNF Neuberger, Freiburg, Germany) with two heads in series up to 17 bar into the 20 L SS cylinders (originally lpg tanks, Crwion SAheet Metal, Invercargilol, New Zealand). The sampling time for one sample amounted to about 20 min, covering a distance close to 250 km. A predecessor high-pressure air-pumping

system developed for Antarctic flights on US navy aircraft[13] was not compatible with passenger aircraft.

Air sampling took place at preset intervals during the outbound flight. During the subsequent return flight, fresh samples were taken by replacing the outbound samples one after the other. The reason for sampling twice was that in case of failure of equipment during the return flight, at least samples from the outbound flight were available. In fact, on two flights, equipment on the return flight did not function, and thus samples from the outbound flight were available.

Before the actual sample air collection each cylinder was pressurized and purged several times to 5 bar in flight to flush and condition the cylinders. As ambient temperatures were generally below $-30°C$, the sampled air is basically dry. However, as we will see later, oxygen isotope exchange problems with water occurred. The tanks used had not been electropolished. Inspection of the interior showed some traces of discoloration due to oxidation along the welds. It was not clear beforehand to what degree this medium-pressure compressor system and cylinders for CARIBIC-1 was suitable for CO_2, but, as will be shown below, the measurements were of high quality. For these samples halocarbon measurements and hydrocarbon measurements[14,15] also confirm that the system was free of air leaks and of high purity.

After the collection of air samples the analytical approach detailed below is based on three processes, namely (i) quantitative trapping of CO_2 (including N_2O and other condensable trace gases, i.e. CH_3Cl and NMHC,[16] followed by quantitative recovery; (ii) final drying of recovered CO_2; (iii) off-line use of a symmetrically configured dual-inlet isotope ratio mass spectrometer, i.e. the traditional method of analysis.

CO_2 extraction and drying

Upon return of the container to the institute after its monthly set of flights, the 150 kg sampling system was removed from the container and connected to the trace gas extraction system in a laboratory on the second floor of the building via a ¼″ SS tube of about 15 m length. Sample processing took place over a period of three consecutive ~10 h days, always immediately after landing. Prior to extracting the large volume samples, at least two aliquots of ~6 L air each were expanded into electropolished SS canisters and stored.

The sample processing procedure was initially developed for the extraction of the CO content (between 15 and 150 μL) for stable isotope and ^{14}C analyses. The CO extraction by means of CO oxidation on Schütze reagent (I_2O_5 on acidified silica gel), followed by cryogenic trapping of the CO_2 produced from CO,[17] requires quantitative (over 99.9999%) stripping of the CO_2 content prior to the CO oxidation step. Thus, high-efficiency cryogenic traps with borosilicate-glass filters (Russian Doll Traps, RDTs[10,11]) are used. After having trapped the condensable gases (CO_2, N_2O, H_2O and trace amounts of NMCH and halocarbons) during the processing of a sample (~300 L STP air) the first RDT (which contains well over 99.9% of all CO_2 and condensable gases) was evacuated while still submerged in liquid nitrogen. Subsequently, the liquid nitrogen was withdrawn and the condensables were distilled into a U-tube trap immersed in

liquid nitrogen. During this time, the temperature of the RDT rose slowly but remained well below the freezing point. After the pressure had dropped to a stable low level close to ~1 Pa, distillation was terminated prior to the onset of a second pressure rise due to water release. The procedure took 30 min. Next, the condensable gas mixture was frozen and expanded into a ~100 mL bottle with a few grams of P_2O_5 for final drying (tests over 24 h show that P_2O_5 does not induce ^{18}O exchange, in contrast to magnesium perchlorate, drierite ($CaSO_4$) and silica gel) and finally transferred to a ~100 mL glass bottle for isotope analysis. Having performed CO_2 isotope measurements, the extracts (~100 cc STP each) were finally flame-sealed in glass ampoules for future isotope analyses (e.g. $^{14}CO_2$, ^{13}C, D in CH_3Cl). More than 300 of these extracts are available. A short description of the gas extraction line and tests for RDT traps is given by Pupek *et al.*[16]

For the first process, trapping and release, the stated efficiency for trapping of over 99.9% is based on extensive experience with CO extractions. The breakthrough of CO_2 was estimated in this way to be well below 1 ppbv, or ~3 ppm of the total CO_2 content. Because this was based on two RDTs in series, and only CO_2 trapped in the first RDT is used here, less than 0.17% of the original CO_2 is expected to have escaped. This is an upper limit based on routine use, and if any bias occurred this would be systematic. Dedicated tests using only one RDT show that the trapping efficiency of one single trap is over 99.99%. Independently, Pupek *et al.*[16] tested how much CO_2 broke through RDT-1 and was trapped in RDT-2. By isolating RDT-2 and recovering all gases trapped here, they found that less than 0.03% of all CO_2 escaped from RDT-1. The high efficiency of these traps is based on four nested borosilicate glass fibre thimbles.

Considering the trapping efficiency to be beyond dispute (which means no isotope effects due to CO_2 trapping), the full release of CO_2 trapped may be a concern. The question is if any CO_2 is retained on the large surface area of borosilicate when the sample CO_2 is collected from the trap. Again our experience with CO extractions helps. In this case, amounts of as little as 10 μL of CO_2 (derived from oxidation of CO) are trapped and released from a similar RDT. Even if this were at an efficiency of only 90% and 1 μL was lost due to long-term trapping, this would amount to a loss of only 0.001% for the air-CO_2 samples. This means that there is no significant CO_2 residue on the RDT.

Concerning the second point, drying, we note that CARIBIC sample air is dry to very dry compared with boundary layer tropospheric air samples. A complete set of humidity data for CARIBIC I is not available, but the statistics of CARIBIC II, flying at the same altitudes based on almost 700 air samples, show an average H_2O mixing ratio of 170 ppmv. This corresponds at 20°C to a relative humidity of 0.44%. Only 4% of the samples had over 1000 ppmv, and 29% over 100 ppmv. Although this air is compressed to 17 bar, no saturation and condensation will take place at normal temperatures (about 20°C). The air released from the sample cylinder has exactly the same humidity. Based on that and also on requirements for other gas analyses, no drying agent was used. However, as will be shown below, H_2O-CO_2

isotope exchange in cylinders persisted for a long time, meaning that some water remained active.

The recovered CO_2 was dried in two steps. One is the retention of H_2O in the collection RDT, the other is drying of the extracted CO_2 with P_2O_5. The retention of H_2O in the RDT could be closely followed by observing pressure variations in the Pa range. There always were two pressure surges; one very large one for CO_2 and a second small one for H_2O. This latter started slowly, after the first peak had dropped to below 1 Pa. Before this second increase, the transfer was terminated.

The final drying using P_2O_5, as stated, has been shown in 24 h long experiments not to allow any oxygen isotope exchange. [We note in this respect that the Schütze reagent itself (I_2O_5 on H_2SO_4-acidified silica gel), which is used to oxidize CO to CO_2, is also therefore successful in that it does not change the oxygen isotopic composition of the CO_2, although the amount of the Schütze reagent is very large, at about 1 L of material (the acidity of P_2O_5 and the various acids that are formed when drying excludes isotope exchange via bicarbonate)]. A final aspect to be considered in this respect is that oxygen isotope exchange could possibly occur in the RDT during its release. Sources of exchangeable oxygen are the borosilicate glass itself and the original water vapour in the sample air frozen on borosilicate filters. Between runs the RDTs were, however, flushed for many hours with ultra-dry air. Experience with the trapping of the μL quantities of CO_2 derived from CO also shows that exchange on borosilicate filters is fully absent. As stated, CO_2 release took place while the temperature of the RDT remained well below freezing point. Although the exchange with water frozen on the borosilicate filters (large surface) has not been explicitly studied, we know that the oxygen exchange between CO_2 and H_2O at low temperatures in snow/firn takes years to occur.[18] It can, therefore, be concluded that the degree of oxygen isotope exchange with water present in the sample air during trapping, release and subsequent drying is negligible. No other oxygen isotope exchange processes could be identified.

As mentioned before, additional information about the functioning of the extraction system is based on values from tests made using hydrocarbon and halocarbon measurements of the extracts compared with the original values. For these tests, the direct measurement of these compounds on the air samples was compared with the same analyses based on diluting the extracted condensates with zero air.[16] The tests show satisfactory recovery of the lighter hydrocarbons and halocarbons. Thus, trapping and release of such compounds, even at sub-ppbv concentrations, were quantitative, although with a margin of 10%. Although such tests cannot provide explicit information as to the suitability of the extraction procedure for CO_2, they give a high degree of confidence in the procedure.

Considering the large amounts of CO_2 involved, the high efficiency of the RDTs, the control of processes based on the results obtained for CO (concentrations of down to 40 ppbv) extractions and isotope measurements of CO, it is extremely unlikely that there have been any systematic biases that affected the $\delta^{13}C$ and $\delta^{18}O$ values of the CO_2 extracted.

IRMS measurements and calibration

Having large samples of dry clean CO_2 ($\sim$100 cm^3) the next task is to achieve accurate, precise isotope ratio mass spectrometry (IRMS) measurements traceable to the VPDB-CO_2 scale based on NBS-19-CO_2. The MAT 252 mass spectrometer used (ThermoFinnigan, Bremen, Germany) is equipped with a dual viscous flow inlet system (and automated micro volumes for small samples). The inlet system was pumped by means of a separate turbo-molecular pump-diaphragm pump combination. Highest accuracy measurements of stable isotope ratios of CO_2 are based on a fully symmetrical inlet system. The standard and reference gases are introduced via identical systems having identical valves, bellows, and capillaries at identical temperatures. With equal gas pressures on both sides, equal signals for mass 44 (typically 4.5 V, signals adjusted to within 50 mV) were obtained. Thus both capillaries are crimped to identical degrees. Measurements of delta values with the same gas in both bellows (zero enrichment measurements) repeatedly give values within $\pm$0.012 and $\pm$0.020‰ and better (for $\delta^{45}R$ and $\delta^{46}R$, respectively) which correspond to typical internal precisions (2-σ values). Tiny differences between the two sides could not be fully excluded in that respect that the amount of gas differed in practice. These differences of up to 30% are not relevant because large amounts were always present on both sides with $\sim$50% compression of the bellows while the actual gas consumption was less than 0.5%. Moreover, the ion source was always tuned for a high linearity, of typically better than 0.020‰/V and 0.040‰/V for $\delta^{45}R$ and $\delta^{46}R$, respectively.

The ion source operated at 10 kV is known to cause a certain degree of $\delta^{45}R$ and $\delta^{46}R$ scale contraction due to cross-contamination via a memory effect in the ion source.[19,20] The cross-contamination factor η is given as:[19]

$$\delta_{\text{meas.}} = \delta_{\text{true}} [1 - 2 \cdot \eta - \eta \cdot \delta_{\text{meas.}}] \qquad (1)$$

with

$$\eta = [\delta_{\text{true}} - \delta_{\text{meas.}}]/[\delta_{\text{true}} \cdot (2 + \delta_{\text{meas.}})] \qquad (2)$$

For small values of $\delta_{\text{meas.}}$, Eqn. (2) may be approximated as:

$$\delta_{\text{true}} \approx \delta_{\text{meas.}}/[1 - 2 \cdot \eta] \qquad (3)$$

The cross-contamination magnitude was first minimized by keeping the variable ion source conductance window fully open. As the light CO_2 working reference (WR) gases in use did not match the isotope composition of the CO_2 samples, the correction was significant as shown below. Since May 2001 the cross-contamination has been regularly determined by analyzing the two WR-CO_2 gases with their large isotope difference ($\delta^{45}R_{\text{WR1}}$WR2 and $\delta^{46}R_{\text{WR1}}$WR2 of $\approx$38.8 and 14.7‰, respectively), and idle times (flushing after changing-over from WR-CO_2 to sample, and vice versa) varied, namely 30, 180 and 300 s. As all the measurements before May 2001 were performed under identical conditions (no filament replacement, no re-tuning), the same values for η were applied backward to the data obtained before May 2001. In March 2002 the cross-contamination was greatly reduced by installing an ion source slit made of tantalum, which reduces the effect.[21] Before installing the Ta slit in March 2002 the factor η was $\approx$0.0008 and $\approx$0.0010 (for

$\delta^{45}R$ and $\delta^{46}R$, respectively). After installing the ion source slit in March 2002, the values were at least 50% lower.

Our calibration scale has been maintained by two machine working reference gases of CO_2 (WR-CO_2) of high purity. One was stored in a high-pressure cylinder and at 3 bar in a 21 L SS cylinder connected to the reference bellows variable volume of the MAT 252 mass spectrometer via a manifold with valves. The other (also a high-pressure cylinder), initially only available from two $\sim$1 L glass flasks, was later also supplied via a second 21 L SS cylinder at 3 bar to the reference bellows. This approach ensured the long-lasting integrity of the WR-CO_2 gases. The reproducibility and refilling integrity were checked extensively by analyzing a number of separate aliquots stored in glass flasks (two flasks for each WR-CO_2).

As stated, the samples were measured vs. two WR-CO_2 gases – light CO_2 ($\delta^{13}C \sim -42.6$‰) and heavy CO_2 ($\delta^{13}C \sim -3.2$‰). Before March 2002 (old ion source slit, high values of η), the corrections for the raw data obtained vs. isotopically light WR-CO_2 were $\sim$0.06‰ for $\delta^{45}R$ and $\sim$0.07‰ for $\delta^{46}R$. Smaller corrections, namely $\sim$0.008‰ and $\sim$0.03‰, respectively, were applied when the samples were measured vs. the isotopically heavier WR-CO_2. After March 2002 with the Ta slit installed the correction magnitude has been reduced to 50% and less of its initial magnitude. Because the $\delta^{13}C(CO_2)$ and $\delta^{18}O(CO_2)$ values obtained on the same sample vs. the two WR-CO_2 gases are in very good agreement (see below) this proves that correction magnitudes have been determined and applied correctly.

The measurement procedure included a peak centring, signal adjustment, five change-over sequences between sample and WR-CO_2 (idle time of 30 s and integration of 4 s) as well as interfering mass measurement on m/z 18, 28, 29 and 30 (these are H_2O, N_2 and fragment ions of N_2O and CO_2). The levels of H_2O and N_2 were nearly always stable and low. If these levels were high, the mass spectrometer capillaries were baked out and measurements were repeated. Typical standard errors for $\delta^{45}R$ and $\delta^{46}R$ ($n = 5$, 95% level) were $\pm$0.012‰ and $\pm$0.020‰. Although the MAT 252 measurement procedure and the composition of WR-CO_2 gases were not optimized for the highest accuracy possible for CO_2 samples (the low number of sample/WR switches as well as the composition of the light WR-CO_2), a careful revision of the calibration and corrections does provide high-quality CO_2 isotope data.

The WR-CO_2 gases were calibrated using five extractions of NBS-19-CO_2 (H_3PO_4 acid digestion at 25°C), see Table 1. This calibration was verified by analyzing NIST RM 8562 and RM 8563 CO_2 gases in glass break-seals – $\delta^{13}C(CO_2)$ and $\delta^{18}O(CO_2)$ obtained (Table 2) appeared to be in excellent agreement with the values reported by Verkouteren.[22] The agreement confirms both our calibration and the accuracy of the cross-contamination correction, with excellent agreement of values obtained vs. two distinct WR-CO_2 gases (Table 2). Because $\delta^{18}O(CO_2)$ values determined on NIST RMs agree well with the published values within their uncertainty of $\pm$0.11‰ (Table 2) and the difference is lower than the standard error of our $\delta^{18}O(CO_2)$ calibration vs. NBS-19-CO_2 (around 0.20‰, see Table 1), our $\delta^{18}O(CO_2)$-calibration uncertainty has been adopted, based on analyses

Table 1. Calibration of WR gases. Standard error at the 95% level

WR gas in use	$\delta^{45}R$ of NBS-19-CO_2 vs. WR gas, ‰	$\delta^{46}R$ of NBS-19-CO_2 vs. WR gas, ‰	$\delta^{13}C^*$, ‰ VPDB-CO_2	$\delta^{18}O^*$, ‰ VPDB-CO_2
WR-CO_2-1	44.301 ± 0.015	27.90 ± 0.19	-42.504	-29.22
WR-CO_2-1 (refilled, valid from September-4-2001)	44.361 ± 0.016	27.83 ± 0.19	-42.564	-29.16
WR-CO_2-2	5.275 ± 0.014	12.05 ± 0.20	-3.259	-14.08
WR-CO_2-2 (refilled, valid from August-11-2001)	5.086 ± 0.013	12.27 ± 0.20	-3.051	-14.30

* $\delta^{13}C$ and $\delta^{18}O$ values (calculated by the IAEA-recommended algorithm[23]) are given for indicative purposes only. They were not used for the actual calculations.

of the NIST RMs as ± 0.12‰. Measurements of the NARCIS-1 and NARCIS-2 plain CO_2 gas also demonstrated good inter-laboratory agreement.

The integrity of the two WR-CO_2 gases in the 21 L SS cylinders was regularly checked by measuring aliquots of these gases stored in several 1 L glass flasks. Measurements of the same gas stored in a different flask as well as measurements of the two WR-CO_2 gases against each other demonstrated no systematic drift.

Corrections for N_2O and ^{17}O

After correction of the raw measurement data ($\delta^{45}R$ and $\delta^{46}R$) for the cross-contamination, the subsequent corrections were carried out: (1) scaling the resulting $\delta^{45}R$ and $\delta^{46}R$ values to NBS-19-CO_2 by using $\delta^{45}R$ and $\delta^{46}R$ measured for WR-CO_2 vs. NBS-19-CO_2 (Table 1); (2) expressing absolute values of ^{45}R and ^{46}R by using the IAEA-recommended ^{13}R, ^{17}R and ^{18}R ratio set[23] and $\delta^{13}C = 1.95$‰ and $\delta^{18}O = -2.20$‰ assigned to NBS-19-CO_2;[25] (3) numerically solving the equations for ^{46}R and ^{45}R in terms of ^{18}R and ^{13}R values and then expressing them as ^{13}C and ^{18}O; and (4) correcting $\delta^{13}C$ and $\delta^{18}O$ for the N_2O contribution. The ^{17}O-correction incorporated in our data treatment spreadsheet was tested to produce the same $\delta^{13}C$ and $\delta^{18}O$ as the interactive web-tool[26] maintained by NIST.[27] By using this spreadsheet, data after another ^{17}O correction may be easily generated.

The N_2O correction assumes that the $\delta^{13}C$ value (like $\delta^{18}O$) obtained on a sample is a linear combination of $\delta^{13}C(CO_2)$ and $\delta^{13}C(N_2O)$ in proportion to the N_2O/CO_2 ratio scaled by E_{N2O}, the N_2O relative ionization efficiency (see[28,29]) according to:

$$\delta^{13}C_{meas.} = \delta^{13}C(CO_2) + \delta^{13}C_{app}(N_2O) \cdot [N_2O]/[CO_2] \cdot E_{N2O} \quad (4)$$

The N_2O and CO_2 mixing ratios in the samples were measured using high-precision gas chromatography/electrochemical detection (GC-ECD) techniques and are reported on the NOAA/ESRL scale. The value of E_{N2O} determined on our MAT 252 mass spectrometer on pure N_2O compared with CO_2 (filled in the same bellow to the same pressure) was slightly variable around 0.71 over a period of several years. It has been reported that E_{N2O} determined on pure gases can deviate from the effective value characterizing the N_2O behaviour in CO_2+N_2O air mixtures,[29–31] but for our MAT 252 the deviation appeared to be not significant, as shown below. In a dedicated study,[31] Assonov and Brenninkmeijer found that the ratio of best-fit lines for N_2O- and CO_2-pressure dependence gives an apparent value of $E_{N2O} = 0.686$ and the effective value found on N_2O-CO_2 mixtures by using the fragment ions at m/z 30 is 0.687. That means a 3.5% difference in the N_2O correction magnitude.

We note that for data compatibility we use the values of $\delta^{13}C_{app}(N_2O) = -343$‰ and $\delta^{18}O_{app}(N_2O) = -497$‰[28] as used by other labs, although Assonov and Brenninkmeijer[31] found that the value of -343‰[28–30] is in error by -15‰.

Finally, we note that a new type of N_2O correction was developed[31] based on the fragment ions of CO_2 and N_2O at m/z 30. When this new N_2O correction is applied to the CARIBIC-1 data, the discrepancy with the data produced by the standard mass-balance approach above is found to be less than ± 0.01‰ for $\delta^{13}C_{app}(CO_2)$ and ± 0.015‰ for $\delta^{18}O_{app}(CO_2)$ (see Fig. 10 in Assonov and Brenninkmeijer[31]). This discrepancy is within the error budget that we describe next.

Error budget

The operating procedures for isotope analyses during CARIBIC-1 had been optimized for CO and CH_4 analyses and were not optimal for highest accuracy air-CO_2

Table 2. Verification using NIST RM 8562 and RM 8563 CO_2 and NARCIS CO_2. Standard error at the 95% level

RMs	Obtained $\delta^{13}C^*$, ‰ vs. VPDB-CO_2	Published[22,24] $\delta^{13}C^*$	Obtained $\delta^{18}O^{***}$, ‰ vs. VPDB-CO_2	Published[22,24] $\delta^{18}O$
RM 8562 vs. light WR-CO_2	-3.778 ± 0.020	-3.76 ± 0.03	-18.56 ± 0.20	-18.51 ± 0.11
RM 8562 vs. heavy WR-CO_2	-3.763 ± 0.017	-3.76 ± 0.03	-18.52 ± 0.20	-18.51 ± 0.11
RM 8563 vs. light WR-CO_2	-41.547 ± 0.021	-41.56 ± 0.06	-33.68 ± 0.20	-33.63 ± 0.11
RM 8562 vs. heavy WR-CO_2	-41.536 ± 0.020	-41.56 ± 0.06	-33.65 ± 0.20	-33.63 ± 0.11
NARCIS-1	-8.557 ± 0.020	$-8.549 \pm 0.032^{**}$	-0.630 ± 0.20	$-0.679 \pm 0.130^*$
NARCIS-2	1.914 ± 0.020	$1.923 \pm 0.020^{**}$	-2.554 ± 0.20	$-2.558 \pm 0.112^*$

* For comparison reasons, $\delta^{13}C$ values are calculated using the IAEA-recommended algorithm.[23]
** Mean of the data from seven labs given as 2 St.Dev.
*** Errors given for $\delta^{18}O$ are based on calibrations vs. NBS-19-CO_2 (Table 1); this aspect was reconsidered later, see text.

measurements (the isotopic composition of the depleted WR-CO_2 was optimized for CH_4 and CO and the number of change-over sequences was restricted to five in order not to waste the limited amount of CO_2 produced by CO and CH_4 extractions). However, by paying special attention to all relevant factors involved, the data that we obtained are reliable and of good quality. Although the ^{13}C isotopic composition of the two WR-CO_2 gases differed significantly from that of atmospheric CO_2 (Table 1), the correction for cross-contamination was carefully determined and applied. Here we do not expect undue uncertainties to have been introduced. Because the standard errors are calculated on the basis of only five change-over sequences between sample CO_2 and WR-CO_2 this practice might underestimate the real instrumental uncertainty.

The total combined uncertainty comprises not only the uncertainty of the IRMS measurements, of corrections for cross-contamination and N_2O, but also the calibration uncertainties of the two WR-CO_2 gases in use and their long-term integrity. Although we have not performed special tests aimed at evaluating a total uncertainty (e.g. inter-laboratory comparisons), we can evaluate our results based on the differences of the two large data sets that we obtained by measurement for all 318 samples vs. two fairly different WR-CO_2 gases.

For $\delta^{13}C(CO_2)$ there is no bias (Fig. 1, left) and 95% of all deviations (here absolute values are taken) are less than 0.041‰. Close inspection shows a minor skewing of less than −0.01‰. However, one can use 0.041‰ as 2-σ or 0.020‰ as 1-σ value that characterizes data scatter due to all analytical steps including the mutual calibration consistency of two WR-CO_2 gases, limited number of change-over cycles as well as possible fluctuations in cross-contamination magnitude and E_{N2O} on different days. This thus gives the combined uncertainty due to all analytical steps. The value does not include the calibration uncertainty itself because one could have a calibration bias but still observe a mutual agreement

in the data obtained vs. two WR-CO_2 gases. However, the bias is basically excluded as a good agreement with published values was obtained on pure CO_2 gases of various isotope composition (Table 2).

For $\delta^{18}O(CO_2)$ there is a bias of about 0.015‰ (Fig. 1, right). This implies a small inconsistency in corrections of, for instance, the cross-contamination. However, because the data bias of 0.015‰ is less than the total combined uncertainty evaluated, we do not apply any data re-analyses. For $\delta^{18}O(CO_2)$ the 95% level of the distribution (Fig. 1, right, absolute values are not plotted) gives 0.065‰ which we use as the 2-σ value.

Finally, we calculate the mean of the two values for $\delta^{13}C(CO_2)$ and $\delta^{18}O(CO_2)$ obtained for each sample vs. the two WR-CO_2 gases. The estimated *total combined uncertainties* are calculated to be ±0.044‰ and ±0.125‰ (95% level), respectively, which includes both the calibration uncertainty and the analytical uncertainty as evaluated from the data distribution in Fig. 1. The calibration uncertainty for $\delta^{18}O(CO_2)$ is based on the measurements of RM 8562 and RM 8563 (Table 2, see above).

Here we emphasize that obtaining consistent $\delta^{13}C(CO_2)$ data sets vs. two WR-CO_2 gases signifies a rather critical and self-consistent test. The first WR-CO_2 has a $\delta^{13}C(CO_2)$-difference relative to air-CO_2 of −34‰ while the second WR-CO_2 has a difference of +5‰. For $\delta^{18}O(CO_2)$ the differences are lower at −29 and −14‰, correspondingly.

$\delta^{18}O(CO_2)$ shifts in the sampling cylinders and quality of isotope data

The CO_2-water isotope exchange in sampling canisters or flasks is discussed as the major problem of sampling (e.g.[32–34]), especially when samples are collected without drying. Disagreement in the $\delta^{18}O(CO_2)$ values for air samples taken in duplicate at a given location is considered to indicate water-CO_2 oxygen isotope exchange and such data are discarded (e.g.[34]). In the case of large $\delta^{18}O(CO_2)$ shifts, the $\delta^{13}C(CO_2)$ values may also be affected and discarded. To avoid the problem, glass or SS sampling canisters are generally preconditioned by heating, either under vacuum or while being flushed with dry air. Moreover, drying agents are used to dry the samples.

The large SS CARIBIC cylinders were neither preheated nor individually tested for CO_2-water exchange. Preconditioning was only achieved by the pressurizing-purging sequence prior to the actual sampling. As stated before, ambient air at cruising altitude is cold (−30 to −60°C) and has a low content of water (super-saturation is not rare but the absolute amount of water is still very small compared with that in tropospheric samples. Even the compression to 17 bar does not lead to condensation). Despite this, the $\delta^{18}O(CO_2)$ values were in many cases corrupted by exchange with water. [CO_2 exchanged with water is expected to have negative $\delta^{18}O$ (VPDB-CO_2 scale) because: (1) tropospheric water vapour has negative $\delta^{18}O$ (VSMOW scale) and (2) CO_2-water exchange gives $\delta^{18}O(CO_2)$ at ∼41 ‰ higher than the water value.] Two processes occurred and are illustrated here.

First, the $\delta^{18}O(CO_2)$ values demonstrated a systematic trend with time. $\delta^{18}O(CO_2)$ values obtained before May-3-
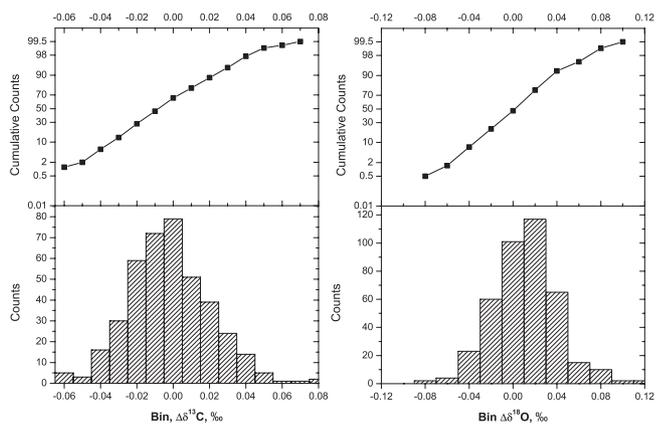
Figure 1. The distribution of the difference between $\delta^{13}C$ (left) and $\delta^{18}O$ (right) values obtained vs. the two WR-CO_2 gases used. The scatter is due to random fluctuations of values such as analytical uncertainty, drift of parameters for the cross-contamination correction, N_2O correction, etc. Analysis is based on all 318 CARIBIC samples from 28 flights measured vs. two WR-CO_2 gases.

1999 (flight #11) showed a large scatter and the values are also much below the natural level expected. After May-3-1999 the scatter decreased. This reduction must be purely a matter of conditioning of the sample cylinders because the destination of the aircraft did not change.

The second observation is that the $\delta^{18}O(CO_2)$ effect is cylinder-specific: cylinders #1, #6, and #9 systematically demonstrate negative values (below $-1‰$) while other cylinders demonstrated $\delta^{18}O(CO_2)$ close to or above $0‰$ (Fig. 2(b)). Repetitive sampling of humid areas in the same cylinders can be excluded as a cause as the behaviour is reproduced for samples from different flight routes.

The magnitude of the 'water effect' decreased with time, and all the $\delta^{18}O(CO_2)$ values obtained after October-18-2000 (flight #28) have a compact distribution around $0‰$ or above (Fig. 2(a)). After October-18-2000 the scatter, given as 1 St.Dev. of the 12 sample set from a single flight, was not more than $0.185‰$, the spread in values was not more than $0.65‰$. All samples taken within a single flight at that time have similar $\delta^{18}O(CO_2)$ values, implying negligible or at least a very similar magnitude of the 'water effect'. However, even after October-18-2000 the cylinder-specific effect can still be observed, although in a weakened form (Fig. 2(c)). We note that since we acquired our cylinders from Crown Sheet Metal in the early 1990s, they have developed such cylinders for scientific purposes.

We applied an arbitrary quality filter for all the $\delta^{18}O(CO_2)$ values: values below $-1‰$ have been discarded (total of 42 data points). All the $\delta^{18}O(CO_2)$ values obtained after October-18-2000 that are above $-1‰$ are considered to be reliable. Selecting another cut-off limit (e.g. $-0.5‰$) would shift the $\delta^{18}O(CO_2)$ data pool only a little. $\delta^{13}C(CO_2)$ is much less sensitive to CO_2-water exchange than $\delta^{18}O(CO_2)$, and $\delta^{13}C(CO_2)$ values corresponding to $\delta^{18}O(CO_2) \leq -2.0‰$ have been discarded (total of 19 data points).

Figure 2. (a) CARIBIC $\delta^{18}O$ values exhibit a large spread from the beginning of the project and a narrowing of the distribution after May 3, 1999. After October 18, 2000, the scatter is significantly reduced and it can be assumed that no CO_2-water exchange occurred. (b) $\delta^{18}O$ values plotted vs. aircraft cylinder number. A distinct 'cylinder effect' is observed: while cylinders #1, #6 and #9 demonstrate $\delta^{18}O$ shifts larger than other cylinders, this effect also persisted for longer times. The $\delta^{18}O$ data may be subdivided as follows: before flight #11 (May 3, 1999) samples from all cylinders give values below $-1‰$ (VPDB-CO_2) which strongly indicates exchange in the cylinders. After flight #11, only three cylinders (#1, #6, and #9) give $\delta^{18}O$ values below $-1‰$, while other cylinders give $\delta^{18}O$ values close to or above $0‰$; after flight #28 (October 18, 2000) the $\delta^{18}O$ values have a compact distribution within one flight. (c) Even after October 2000 (fights 30 to 47), the cylinder effect cannot be excluded completely; negative deviations for cylinders #1 and #9 are visible. Plotted are upper troposphere samples only (stratospheric samples are extra dry and thus not included), for flights 30 to 47.

An independent test of the analytical procedure

To test the whole analytical procedure (extraction as well as measurements, calibration and data corrections), aliquots of two CARIBIC air samples stored in 2.5 L STP SS canisters at $\sim$5 bars for about 1.5 years were sent to the Stable Isotope Laboratory at the Max-Planck-Institute for Biogeochemistry, Jena, Germany. The $\delta^{13}C$ values obtained at MPI-Jena deviate from those obtained on large samples at MPI-Mainz by 0.021 and 0.017‰, respectively, which is within the uncertainty that we expected.
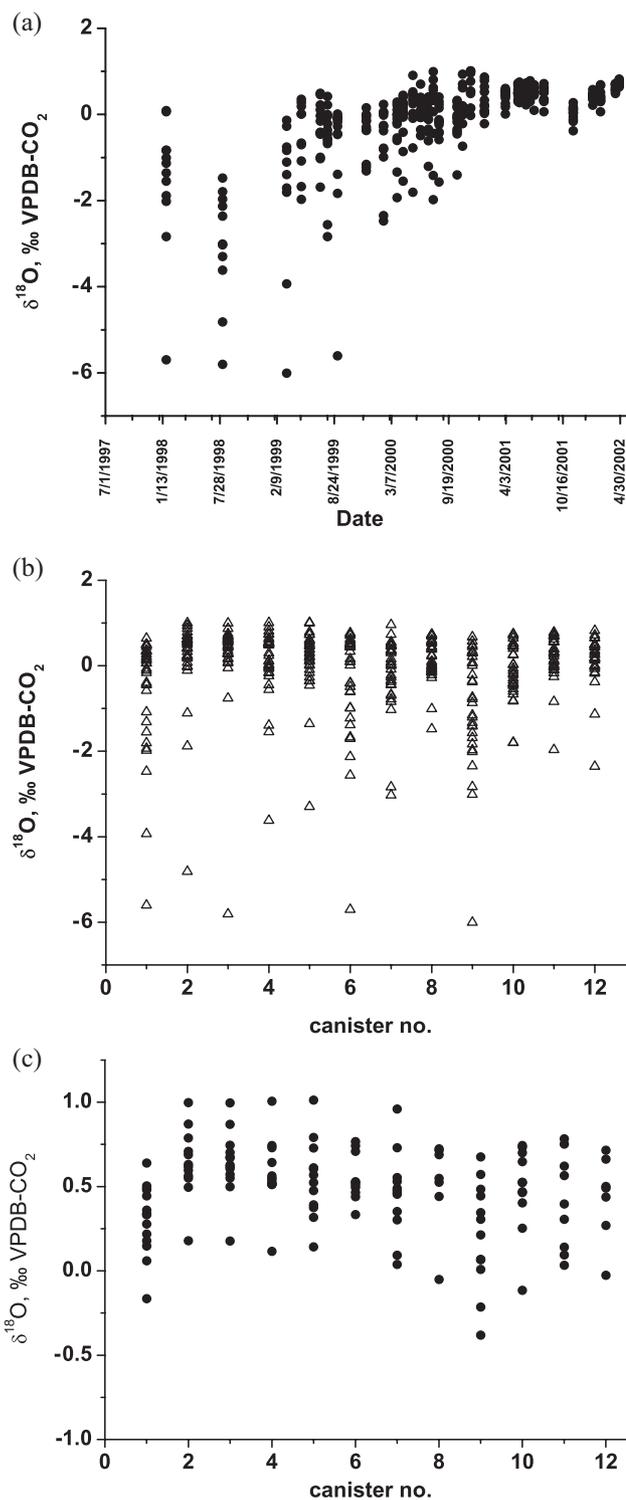
Although the agreement for ^{13}C is excellent this cannot be said for $\delta^{18}O$. The values obtained at MPI-Jena are 0.49 and 0.62‰ lower than values obtained at MPI-Mainz, which is outside the uncertainty range. CO_2-water exchange in canisters which moves $\delta^{18}O$ to negative values is the most likely reason. However, the fact that samples stored for 1.5 years at relatively low pressure (∼5 bar) had to be used, being the only comparison material available, makes it plausible that this part of the comparison is invalid. (Exchange with water as shown for the aircraft sample cylinders does reduce the $\delta^{18}O$ value, see above.)

FINAL COMMENTS

Although conditions in sampling, processing and analysis had not been optimized for CO_2 isotope analysis, the availability of very large air samples, the 100% efficiency of CO_2 extraction using Russian Doll Traps, the effective drying of CO_2 and the use of a symmetric and reliable IRMS system have rendered the data set of high quality. In particular, the systematic use of two working standards that differed considerably in isotopic composition provides an excellent internal quality control. Comparison of performance between a system as described here and common systems widely used elsewhere[35–37] is difficult. For round robin type of inter-comparisons, our demand for air is very high. Other types of inter-comparison during which air is sampled in several flasks at the same time, to be analyzed separately by participating laboratories, are also ruled out by sample size limits. The comparison that we did with MPI-Jena was excellent for [13]C. The discrepancy for oxygen can be attributed to the 1.5 year storage of an aliquot. We further note that oxygen isotope exchange was due to moisture in the cylinders, with some cylinders behaving worse than others.

Oxygen isotope exchange in sampled air is an intrinsic problem. When air masses maintain contact with the ocean or land surface, the amount of CO_2 and its oxygen isotopic composition will change. At the same time more water will be present, basically increasing isotopic exchange. On the other hand small isotope shifts caused in sampling of air masses affected by the surface are less critical. A general criterion for the required quality of the CARIBIC data is the comparison with data from other networks via models.

The internal consistency of CARIBIC-1 data can be demonstrated by compact trends of $\delta^{13}C(CO_2)$ vs. the inverse of the CO_2 content obtained for several flights (Fig. 3). Further, the $\delta^{13}C(CO_2)$ value by CARIBIC-1 at the equator region (latitudes of 0 to 15°N,) shows a good agreement with the trends produced by NOAA/ESRL for ground stations (Fig. 4). The CO_2 content measured by CARIBIC-1 agrees very well with the JAL data for the same latitude band and shows smaller seasonal amplitude than that for NOAA/ESRL ground stations. The smaller amplitude and perhaps some time shifts are due to long-distance air transport and mixing, which also explain why the seasonal amplitude for $\delta^{13}C(CO_2)$ by CARIBIC I is smaller than that for NOAA/ESRL ground stations. [In order to have $\delta^{13}C(CO_2)$-scale consistency with the NOAA/ESRL data set, CARIBIC I data (Fig. 4) are generated using the IAEA recommended [17]O correction algorithm.[23] However, the data can easily be
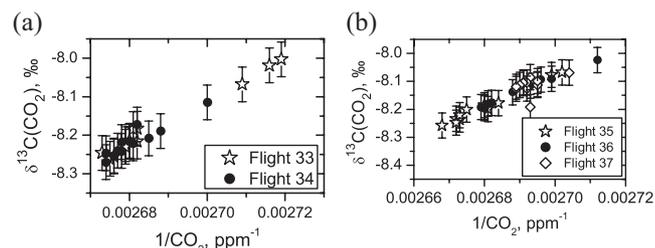
Figure 3. $\delta^{13}C(CO_2)$ values for (upper panel) – flights 33 (stars) and 34 (filled circles); lower panel – flights 36 (filled circles) and 37 (diamonds). The combinations of two fights, corresponding to a limited time interval (about 2 weeks), demonstrate a compact trend of $\delta^{13}C(CO_2)$ vs. the inverse of the CO_2 content. These trends reflect the mixing between the upper troposphere and lowermost stratosphere, as confirmed by stratospheric tracers like ozone (manuscript in preparation).
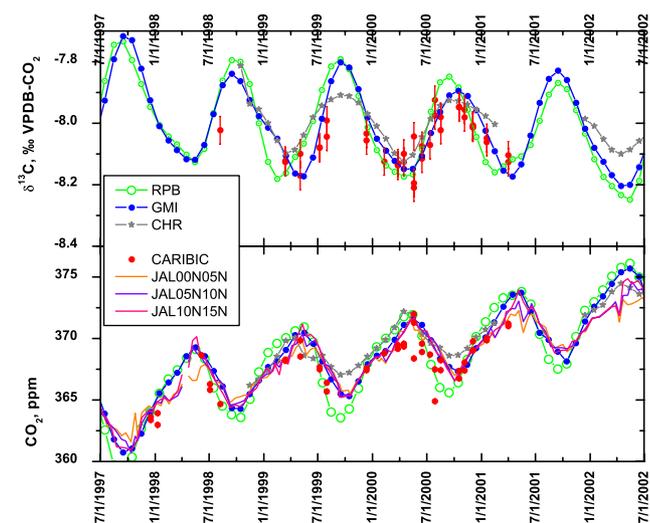
Figure 4. $\delta^{13}C(CO_2)$ data of CARIBIC-1 (latitude band of 0 to 15°N) compared with data produced by NOAA/ESRL ground stations and the JAL project (CO_2 concentrations, latitude bands of 5°). This figure is available in colour online at www.interscience.wiley.com/journal/rcm.

recalculated using the newly recommended algorithm[38] as based on Assonov and Brenninkmeijer.[39]

In a future paper about the system developed for CARIBIC II, attention to inter-calibration issues based on air samples will be given, and attention will also be paid to direct inter-comparison exercises.

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