STABLE ISOTOPE MEASUREMENTS OF ATMOSPHERIC CO_2

J.W.C. WHITE[1,3], D.F. FERRETTI[1], B.H. VAUGHN[1], R.J. FRANCEY[2], C.E. ALLISON[2]

[1] Institute of Arctic and Alpine Research (INSTAAR), University of Colorado at Boulder, Boulder, Colorado, United States of America

[2] Commonwealth Scientific and Industrial Research Organisation — Atmospheric Research (CSIRO), Aspendale, Victoria, Australia

[3] Environmental Studies Program, University of Colorado at Boulder, Boulder, Colorado, United States of America

Abstract. The measurement of stable carbon isotope ratios of atmospheric carbon dioxide, $\delta^{13}CO_2$ are useful for partitioning surface-atmospheric fluxes into terrestrial and oceanic components. $\delta C^{18}OO$ also has potential for segregating photosynthetic and respiratory fluxes in terrestrial ecosystems. Here we describe in detail the techniques for making these measurements. The primary challenge for all of the techniques used to measure isotopes of atmospheric CO_2 is to achieve acceptable accuracy and precision and to maintain them over the decades needed to observe carbon cycle variability. The keys to success such an approach are diligent intercalibrations of laboratories from around the world, as well as the use of multiple techniques such as dual inlet and GC-IRMS and the intercomparison of such measurements. We focus here on two laboratories, the Stable Isotope Lab at the Institute for Arctic and Alpine Research (INSTAAR) at the University of Colorado is described and the Commonwealth Scientific and Industrial Research Organisation — Atmospheric Research (CSIRO). Different approaches exist at other laboratories (e.g. programs operated by Scripps Institution of Oceanography (SIO) and The Center for Atmospheric and Oceanic Studies, Tohoku University (TU)) however these are not discussed here. Finally, we also discuss the recently developed Gas Chromatography — Isotope Ratio Mass Spectrometry (GC-IRMS) technique which holds significant promise for measuring ultra-small samples of gas with good precision.

1. INTRODUCTION

Carbon and oxygen stable isotope ratios of atmospheric carbon dioxide, $\delta^{13}CO_2$ and $\delta C^{18}OO$, provide important, independent information about carbon sources and sinks. Combined with CO_2 mole fraction measurements, the $\delta^{13}CO_2$ measurements can be used to quantitatively separate fluxes between the atmosphere and the terrestrial biosphere from fluxes between the atmosphere and the ocean [6,18,19,20,29]. This is because C3 plants discriminate against $^{13}CO_2$ during photosynthesis while little isotopic discrimination occurs during carbon uptake and release by the ocean. The $\delta^{13}C$ measurements have mainly been used to indicate the one-way carbon fluxes (in the case of fossil fuel release) or net carbon fluxes (e.g. the resultant of photosynthetic uptake and respiratory releases), whereas $\delta C^{18}OO$ measurements more reflect the large (gross) natural cycling of CO_2 between the atmosphere and surface reservoirs, and are only just beginning to be usefully exploited. The two main mechanisms for controlling $\delta C^{18}OO$ on annual to decadal time scales are oxygen isotopic exchange with soil water and oxygen isotopic exchange with leaf water. This isotope can potentially be used to separate photosynthetic and respiratory fluxes for land plants [e.g. 16, 10,7]. Note, the gross fluxes become a complicating factor in $\delta^{13}C$ interpretation when isotopic disequilibria between the atmosphere and surface reservoirs develop (e.g. due to ^{13}C depleted fossil fuel release) and result in second-order $\delta^{13}C$ changes not reflecting net CO_2 exchange, and require careful consideration of response times of exchange [28]. As the atmosphere integrates surface processes over space and time, CO_2 concentration measurements, combined with isotopic measurements, provide constraints for regional scale sources and sinks of atmospheric CO_2 on time scales of months and longer. Indeed, these measurements provide our primary constraints on surface fluxes and thus the processes and

factors, climatic and otherwise, controlling these fluxes. In the future, atmospheric monitoring is also expected to play a central role in verifying any international carbon emission agreements in much the same way that seismic monitoring was used to monitor compliance with nuclear test ban treaties.

The degree to which isotopic measurements made on atmospheric samples are useful is seriously constrained by the precision of the mass spectrometer used. For example, a change of just 0.02 ‰ in $\delta^{13}C$ measured at one site could translate to an equivalent of 1.0×10^9 metric tons of carbon in models of surface fluxes. Such precision is challenging enough on a short-term basis, but this precision is needed over decades if we are to use the data to study trends over longer periods of time. A high precision instrument is required along with diligent, frequent intercalibrations between laboratories.

Here we describe the isotopic measurements made at the Stable Isotope Lab at the Institute for Arctic and Alpine Research (INSTAAR) at the University of Colorado, and briefly refer to different techniques employed at the Commonwealth Scientific and Industrial Research Organisation — Atmospheric Research (CSIRO). The different approaches at these laboratories represents a range of variations in the conventional techniques used to measure the isotopic composition of atmospheric CO_2. Other variations exist, for example the monitoring programs operated by Scripps Institution of Oceanography (SIO) and The Center for Atmospheric and Oceanic Studies, Tohoku University (TU) [19,26]. In addition to discussing traditional dual inlet Isotope Ratio Mass Spectrometry (IRMS) with cryogenic pretreatment of air we also discuss the recently developed Gas Chromatography — Isotope Ratio Mass Spectrometry (GC-IRMS). The latter is less precise than the former but has other attractions such as: smaller sample requirements, no requirement for the N_2O correction due to its contribution of masses 44, 45 and 46, and the elimination of liquid nitrogen use for CO_2 extraction.

2. ISOTOPIC MEASUREMENTS USING DUAL INLET MASS SPECTROMETRY

2.1 Isotopic measurements at the Stable Isotope Lab, INSTAAR

Since 1989, the Stable Isotope Laboratory at INSTAAR, University of Colorado has been measuring the stable isotopic composition of atmospheric CO_2 from weekly flask samples of air obtained from the network of sites operated by the NOAA Carbon Cycle Group, at the Climate Monitoring and Diagnostics Laboratory (CMDL) in Boulder, Colorado. This operation begun with a selection of six sites and two ships in 1990, the measurement effort has grown to include all 55 sites in the CMDL program. During calendar year 1999 over 11,000 isotopic analyses of $\delta^{13}C$ and $\delta^{18}O$ of CO_2 were made at INSTAAR. This included 7,800 sample flasks and 3,200 air standards used for calibration. In 1990 the program began making measurements with a VG SIRA Series 2 dual inlet mass spectrometer. This instrument and extraction system routinely achieved an overall reproducibility of 0.03 ‰ for $\delta^{18}C$ and 0.05‰ for $\delta^{18}O$ (1δ). This includes errors in the extraction process and is determined from replicate measurements of air standards over many years. A Micromass Optima dual inlet IRMS was used beginning in 1996. This machine is fitted with a custom manifold and extraction system, and is used exclusively for making measurements on atmospheric gases. The overall reproducibility for the Optima system is ±0.01 ‰ $\delta^{13}C$ and ±0.03 ‰ for $\delta^{18}O$.

2.1.1 Sample and standard manifold

The automated flask measurement system is composed of three parts: a 40 port manifold; the CO_2 purification system; and the mass spectrometer. The system performs a

number of operations simultaneously (multi-tasks), as one sample is analyzed in the mass spectrometer while CO_2 from the following sample is being purified from the air.

For a measurement run, 20 pairs of 3 L glass flasks are attached to a 40 port manifold using Ultra Torr fittings. The sample flasks used in the NOAA network are Pyrex, taped for safety purposes, and have two stopcocks that allow flushing of the flask when the samples are obtained. Samples are always taken in pairs and filled simultaneously. Results are retained if there is acceptable pair agreement in the isotopic concentrations (discussed below). The flasks are typically over-pressurized by 1.5 atmospheres during sampling, and after other greenhouse gas measurements have taken aliquots, the flasks typically are slightly over one atmosphere pressure when they arrive for isotopic analysis.

Two atmospheric air standards in aluminum tanks AIRCO (BOC Gases Inc, NJ, USA) are also attached to the manifold, using stainless steel tubing (0.0625 in. OD × 0.05 in. ID, with Swaglok-to-VCO fittings), and regulators (High-Purity, Single-Stage, Stainless Steel, model E11-C444A, Air Products and Chemicals, Inc, USA) set to 6 psi. There may be other regulators that can work as well, however, it should be noted that considerable testing led to choosing this regulator over others. For example, a variety of problems have been discovered with regulators that employ Viton seals. Manufacturer's tests for analytical contamination are of limited use, and successful performance of a regulator in this isotopically sensitive system could only be determined by long term testing. This includes extended periods of non-use, to allow for any effects of degassing of sealant materials into the body of the regulator to be seen. Finally a single stage regulator was chosen over a two stage for three reasons: 1) the single stage regulator employs fewer wetted parts, 2) to keep costs down, and 3) a precise outlet pressure is obtained from a two stage regulator is unnecessary, as the flow rate is regulated further downstream by the mass flow controller. Any changes in outlet pressure as the tank drains over time can easily be adjusted.

Air samples from sample flasks or standard tanks enter the manifold through air actuated, low dead volume bellows valves (stainless steel, model SS-6LV-BNBW4, Nupro Company, Willoughby, Ohio, USA). The 14/35 ground glass joints on the flasks seal well with 0.5" Cajon O-ring fittings with thick wall (#2–111, 0.104" thick) Viton-7 o-rings used in place of the standard wall (#2–014, 0.070 in thick) o-rings. Electropolished stainless steel tubing (0.25" O.D. thick wall) is used to connect the flask ports to the Cajon VCO fittings on the manifold.

2.1.2 The CO_2 purification system

Air samples are pulled from the manifold through the extraction system using a rotary vane vacuum pump (model RV-3, BOC-Edwards, Wilmington, MA, USA) at a flow rate of 40 standard cubic centimeters per minute (sccm). The flow is maintained by a mass flow controller (BOC-Edwards, model 825, series B, 0–100 sccm) (Figure 1). During the first minute of air extraction, 40 scc are allowed to waste directly to the vacuum pump, flushing the lines. Following the flush, the sample is then diverted first through a glass water trap, held in an ethanol bath chilled to –85°C by a refrigerated probe (Cryocool, model cc-100, Thermo NESLAB, Portsmouth, NH, USA), and then through a CO_2 trap, cooled to liquid nitrogen temperature. This is basically the Triple Trap extraction system provided by Micromass with two modifications: the addition of a flow controller, and the replacement of the standard water trap with a more efficient one. At the end of the sample extraction time, the flask port is closed, and when the flow rate drops to 10 sccm, a valve is opened that allows the remaining sample air to bypass the mass flow controller (Figure 1).

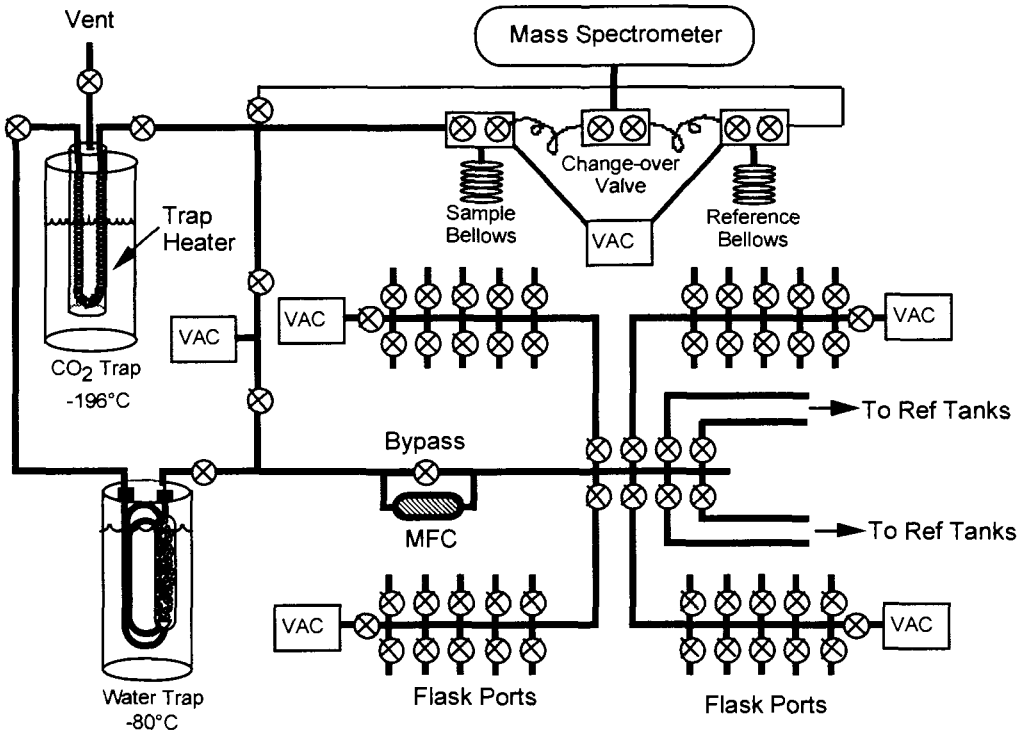

Figure 1. A general schematic showing the flask/reference tank manifold with the extraction system, including mass flow controller, water trap, CO_2 trap, and sample/reference bellows leading to the dual inlet mass spectrometer. The connection from the extraction system to the reference bellows allows large extractions of CO_2 from tank air to be used as reference gas. Tank air CO_2 has isotopic concentrations very similar to flask samples which minimize any gas memory issues in the mass spectrometer source.

As complete removal of water vapor is critical to high precision measurements, and as the efficiency of the water trap determines in part the speed with which air flows though the gas purification system, we use a water trap that employs a number of trapping strategies. The water trap is made of Pyrex with an initial 0.75 in. O.D. vertical section that is filled with glass beads to provide a large, cold surface area (Figure 2a). A 40–60 micron glass frit at the bottom of this section keeps the beads in place and helps prevent ice crystals from escaping this section of the trap. This is followed by two loops of 0.24 in OD glass that are 80% submerged in the ethanol. This section traps and re-traps any water vapor or ice crystals that might have escaped the beads and frit. The glass trap is removable, and is held in place using two 0.25 in. Cajon Ultra Torr fittings. This allows wet traps to be removed and dried offline after each daily run. Traps are dried in a 120°C oven with air circulation to speed the drying time.

The CO_2 trap is modeled after the Micromass Triple Trap, employing a liquid nitrogen bath, and an open-bottomed 2.0 in. O.D. tube surrounding the 'U' shaped sample trap (Figure 2b). The trap is electrically insulated with glass tape, and wrapped with resistive heating wire (~350 cm of 18 gauge, 80% NiChrome wire). With a vent valve on top of the tube closed, the activated heating element boils the LN_2, building N_2 gas pressure in the open bottom tube. This displaces the LN_2, allowing the resistive heating element to further warm the sample to release the previously trapped CO_2.

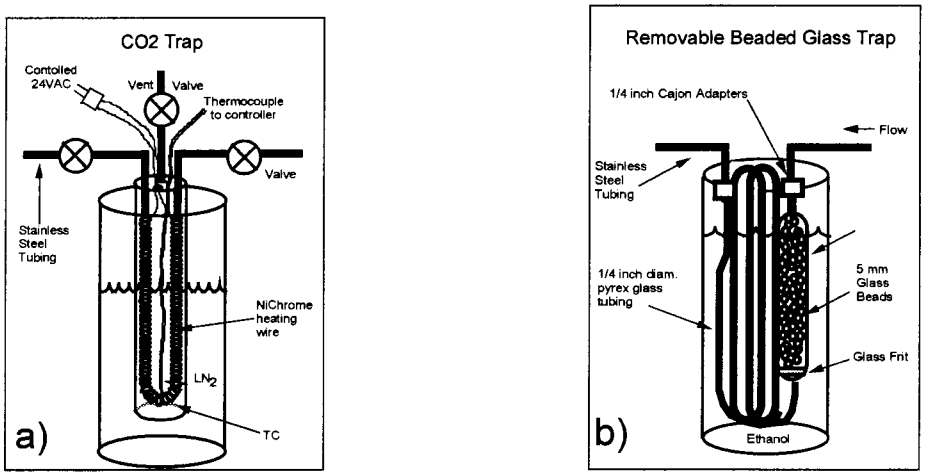

Figure 2. ***a.)*** *The CO_2 trapping system, based on a Micromass design, allows the trap to be alternately controlled to set points of –196°C, –20°C, and +25°C. Liquid nitrogen provides the low point. The warmer temperatures are reached by controlling a NiChrome heating wire (24VAC) on the trap and closing the top vent on the (2 in. dia.) displacement tube. The resulting pressure of gaseous N_2 displaces the liquid N_2 out the open bottom of the displacement tube, allowing further heating.* ***b)*** *The pyrex beaded water trap incorporates an 40–50 micron glass frit at the bottom of a 0.75 in. dia. tube filled with 5 mm diameter beads. There are two open loops that extend out of the chilled bath, to ensure complete removal of water from the air stream by warming and re-trapping of any mobilized ice crystals.*

Once the CO_2 is extracted from the air and frozen in the trap, the system is pumped to high vacuum (5 E-8 mBar) for 60 seconds. Typically, each 400 cm^3 air sample introduced to the system yields ~6.5 δmol CO_2 for isotopic analysis. The isolated sample is then warmed to –20°C and expanded for 60 seconds into the sample bellows. The mass 44 sample beam is then balanced to match the reference target beam to less than ±2% at 5×10^{-9} A.

2.1.3 The mass spectrometer

The mass spectrometer currently used at SIL is a Micromass Optima dual inlet IRMS machine with an electro-magnet. The mass spectrometry is standard. The CO_2 sample and reference gas flow through matched capillary tubes into the source where they are ionized, repelled and accelerated with electric fields and focused into an ion beam. After exiting the source, the ion beam is deflected by the magnetic field, directed into Faraday cups, where the beam currents are measured for mass 44, 45, and 46. Beam currents are amplified, converted to frequencies, and transmitted to the microprocessor by fiber optic cables. The beams are allowed to stabilize for 60 seconds before measurement. The ratios of beams are calculated from integrations taken during 12 reference/sample switches, with outlier rejection (beyond 1 σ). The number of ref/sam switches is determined by two factors. The lower limit is set by the desired internal precision of less than 0.005 ‰ for δ45. This typically requires 8 switches. As the system multi-tasks, extracting one sample while the previous one is being analyzed, additional time is available for switches. The upper limit on switches thus is set by the time required to extract the next sample.

The carbon and oxygen isotope data are reported as δ values relative to VPDB-CO_2, in units of per mille (‰). 0 ‰ VPDB - CO2 = 41.47 per mil VSMOW. The δ notation is given as:

$$\delta^{13}C = [\ (^{13}C\ /^{12}C)_{sam}/(^{13}C\ /^{12}C)_{ref} - 1\ ] * 1000$$

and applies to $\delta^{18}O$ as well.

2.1.4 Data quality checks

Data quality is checked by three mechanisms: flask pair agreement, outlier rejection, and internal standards run as samples. All data is retained and reported so that users can assess data quality. Flags are provided with the data to signify known problems, however, so that data with known problems can be easily removed before the data is used.

Air samples are taken in paired flasks that are filled simultaneously. For all species, data are retained only from those flasks that demonstrate good agreement between each sample pair. The criteria for acceptable pair agreement used at SIL is agreement with three standard deviations, or $|\Delta\delta^{13}C| < 0.03‰$ and $|\Delta\delta^{18}O| < 0.15‰$.

Between trips to the sampling sites, the flasks are filled with dry air with known, but non-atmospheric concentrations and isotopic ratios of CO_2 and other gases. Flasks that are improperly flushed with air can thus be identified and the data flagged. In addition, the data are examined as times series and are routinely filtered for outliers relative to the general trends observed. Such outliers may be real and represent unusual climatic or atmospheric circulation features, for example, or they may represent non-baseline conditions when air was coming from known sources of contamination such as nearby industries, or, in the case of ship board sampling, air blown back from the engine exhaust. Again, such data is flagged, but differently for known problems (as in the case of engine exhaust), as opposed to outliers that deviate significantly from the common trend but that may contain desirable information.

As an internal quality check, SIL began in late 1996 to measure three aliquots of air from a cylinder of air in the middle of each daily run on the mass spectrometer. This additional cylinder, called the "quality control tank" or "trap", is handled in exactly the same manner as the samples, and provides an independent check on the performance of the entire system. The variability of this tank over time is used to determine our overall reproducibility, and problems in the analysis system are frequently first seen and subsequently diagnosed using this trap tank. The recent behavior of the trap tank is shown in Figure 3 and illustrates the value of this quality check. Shown are 10 point running means of the standard deviation (1δ) for $\delta^{13}C$ and $\delta^{18}O$ values of the trap tank. The average standard deviation during the last 160 analysis runs is 0.010 ‰ for $\delta^{13}C$ and 0.042 ‰ for $\delta^{18}O$. Known factors that can cause this number to vary include: source tuning and cleanliness, contamination of the inlet/extraction system by water or organic compounds from gas regulators, and overheating in the CO_2 trap. This latter problem occurs when the autorun sequence stops during heating of the trap to release the CO_2 and the trap temperature exceeds 20°C.

2.1.5 Standards and calibrations

The results are calibrated to external standards, and to internal whole-air references. The internal set of tank-references consists of a hierarchy of 18 aluminum tanks filled with dry atmospheric air obtained from a clean air site located at 4,000 meters elevation on Niwot Ridge in the Rocky Mountains, Colorado, USA. Eight of these tanks are cycled through as the 'daily' reference measurement tank, after first performing as the trap tank. Five more tanks are

measured on a monthly basis, with one tank purposely 'spiked' with $^{13}CO_2$ to be 2‰ different from the others in $\delta^{13}C$. Five other tanks are analyzed every 6 months, with two of those being spiked by 1‰ and 2‰. The tanks are stored horizontally to help minimize any gravitational fractionation, and each tank is assigned its own regulator for the life of the tank air. Multiple tanks are used to guard against any systematic bias resulting from one drifting tank. It is extremely unlikely that any long-term changes in the isotopic concentration experienced by one tank would be identical for all. The structure of a pyramid of standards is essential for providing long-term continuity and precision.

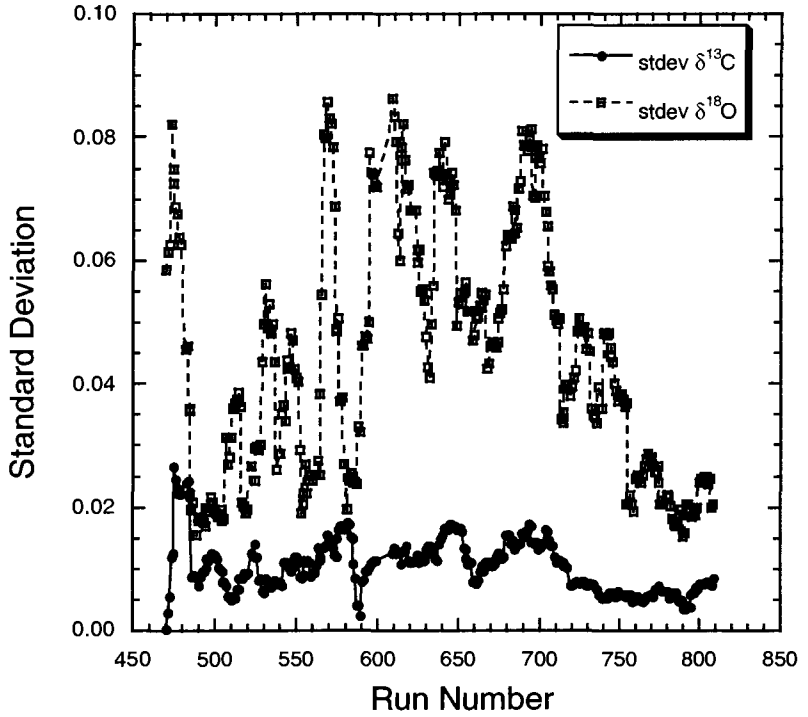

Figure 3. The 10 point running means of the standard deviation of the quality control tank $\delta^{13}C$ and $\delta^{18}O$ as a function of run number.

The standard tanks are tied to the IAEA VPDB CO_2 scale via measurements of carbonates and waters provided by the IAEA and measured by established procedures [9]. As these measurements are made on different extraction systems than the one used for CO_2 in air, we have found that the precision with which air standards can be calibrated to the VPDB CO_2 scale is less than the precision with which air standards can be intercalibrated. Consequently, four labs around the world have been working with the IAEA to resolve internal scale differences and establish air standards for stable isotopes in atmospheric CO_2.

Two types of comparisons between laboratories are maintained as an essential element in the globalization of atmospheric isotopic measurements. The first is an exchange of 5 CLASSIC cylinders circulated by Commonwealth Scientific and Industrial Research Organisation — Atmospheric Research, (CSIRO) among four different labs, including Scripps Institution of Oceanography, (SIO), The Center for Atmospheric and Oceanic Studies, Tohoku University (TU), INSTAAR-CMDL, and CSIRO. Each lab group analyzes the cylinders for CO_2, N_2O, $\delta^{13}C$, and $\delta^{18}O$, and can compare results. While individual labs make their own internal tie to primary carbonate and water (IAEA) standards, the tanks allow very small relative differences between labs to be examined.

The second comparison method between labs is the flask inter-comparison program (ICP). ICP takes an entirely different approach by allowing two or more labs to make measurements on the same flask samples obtained from the same site at the same time, on a regular basis though with lower precision [13,8]. The ICP compliments the cylinder measurements by providing 1) ongoing intercomparisons that allow weekly feedback on sampling and measurement methods, giving laboratories an opportunity to pinpoint problems, and 2) the ICP flask samples are sampled and measured in the same way as the flask measurements themselves, thereby eliminating any potential differences in measurement that may arise from pressurized tanks vs. sample flasks. For example, the ICP program with CSIRO at Cape Grim, Tasmania has identified calibration offsets between the two labs that have led to minor modifications of analysis procedures at both labs. ICP calibrations, combined with rotating tanks such as the CLASSIC tanks, are essential to global integration of greenhouse gas measurements.

2.1.6 Problems with humid air

Drying of air during sampling is clearly important to the quality of the $\delta^{18}O$ measurements, particularly in the relatively small (2.5 L) flasks used in the NOAA network. For samples collected at humid, tropical locations without drying, the $^{18}O/^{16}O$ measurements are highly variable and consistently more depleted in ^{18}O due to the exchange of oxygen atoms between CO_2 and H_2O molecules on the walls of the flasks. Systematic tests at INSTAAR [14] showed that the exchange takes place during storage in the flasks, and that this exchange can occur at humidities less than saturation values. There is also clear dependence on the physical characteristics of each flask. This problem can be seen in the percentage of retained flask pairs, which is much lower for $\delta^{18}O$ (68%) than for $\delta^{13}C$ (94%). The reason for the lower success rate in $\delta^{18}O$ pair agreement is closely tied to the moisture problem, as seen in the trend in low pair agreements at low latitude (generally humid) sites (Figure 4). While seriously contaminated if $\delta^{18}O$ of CO_2 data are obvious (offsets of 4‰), it is impossible to unambiguously determine if $\delta^{18}O$ are slightly affected by exchange with water in the flasks. Consequently, data from 30°N to 30°S are all flagged as suspect. Comparisons of "wet" and "dry" air at several locations indicate that sites outside of this range are not affected.

Field testing of a new prototype air sampling apparatus began at SMO in September 1994 and Cape Kumukahi, Hawaii (KUM) in May 1995. The new AIRKIT (Air Kitzis sampler) differs from the previously used MAKS (Martin and Kitzis Sampler) in two important ways. First, it has a thermoelectrically cooled condenser to remove water vapor from the air stream, and secondly it has a microprocessor to control the sampling process so that collecting the sample is more automated and less subject to operator error. The effect of drying the air sample is most dramatic for the measurement of $^{18}O/^{16}O$ in CO_2. Figure 5 shows the dramatic improvement in the $\delta^{18}O$ values of CO_2 from Seychelles, (Mahe Island, 4° 40' S, 55°10' E) when the switch to using dried air was made in September 1998. There is also speculation that the $\delta^{13}C$ values may be affected by the moisture as well. In autoruns with larger numbers of "wet" flasks, the trap tank value appears to be very slightly shifted in $\delta^{13}C$ (less than 0.003‰). As the precision of the isotopic measurements improves, this suspected problem may become an issue.

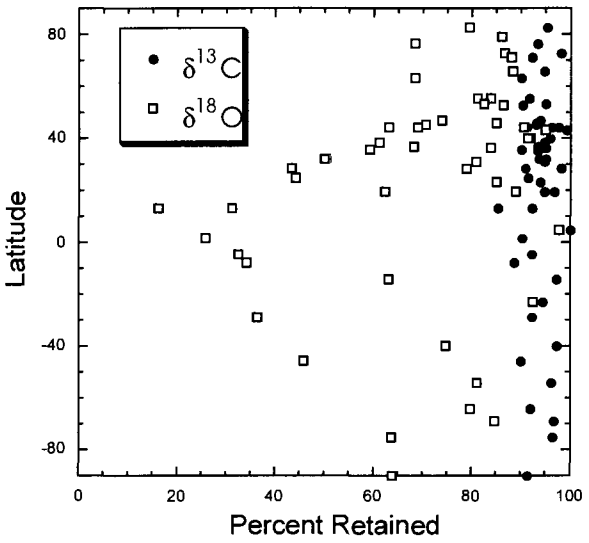

Figure 4. Percentage of flasks from the NOAA network retained for both $\delta^{13}C$ and $\delta^{18}O$ at each site, plotted against latitude. Moisture is a key factor in low retention rates at low latitudes for $\delta^{18}O$.

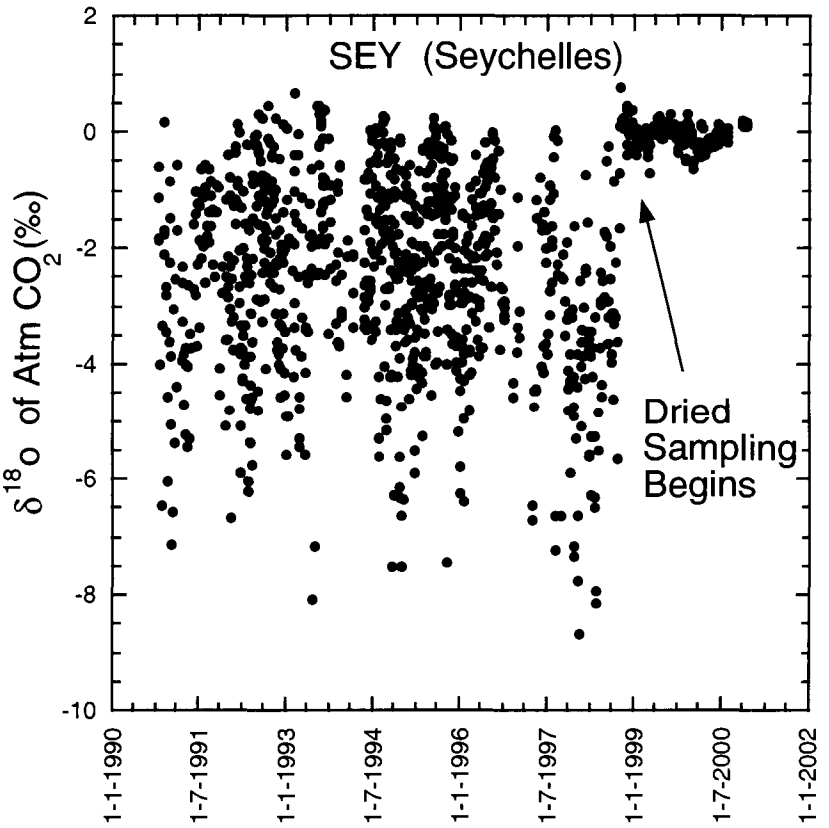

Figure. 5. Oxygen-18 in flask samples from Seychelles (4° 40'S, 55°10' E).

2.2 Isotopic measurements at GASLAB, CSIRO

The long running CSIRO program is documented in a number of technical publications that can be obtained on request, and are briefly summarized here. Two unusual features of the CSIRO program have been: (1) an emphasis on sample drying since inception in 1977, and (2) redundancy in methods of sample collection and sample pre-treatment.

2.2.1 Sample collection and pre-treatment

The Cape Grim *in situ* program commenced in 1977. It involves cryogenic drying, then extraction of CO_2, from around 30 standard liters of air over a two hour period. The extracted CO_2 (about 10 standard ml, 400 μmol) is stored in 100 ml glass flasks fitted with a Teflon o-ring sealed stopcock, and these are returned to CSIRO laboratories at Aspendale for isotopic analysis. Method details, and data from 1982 to the end of 1996 are given in 4 key references [17,18,2].

Flask sampling of whole (dried) air is now conducted from about 13 global sites [15]. A consistent feature of this sampling network has been the chemical drying (magnesium perchlorate) of all flask samples during sample collection. Initially, from 1984, air sampling involved pressurized 5-litre volume glass flasks (8–10 standard liters of air) from 5 sites. The air in the 5 L flasks was completely processed to extract CO_2 with a cryogenic extraction line similar to that used at Cape Grim. The CO_2 samples (about 3 ml, 120 μmol, STP) were stored in 100 ml glass flasks identical to those used for Cape Grim *in situ* samples, until analysis. Since 1992, similarly pressurized 0.5 L glass flasks have been employed, although some 5 L glass flasks are retained for flask storage comparisons. These flasks are processed using a Finnigan MAT (Bremen, Germany) MT Box-C cryogenic separation system that is connected directly to a dedicated inlet of the mass spectrometer system. Typically, 30 ml of air is processed that yields about 10 standard μL (0.4 μmol) of CO_2 for mass spectrometer analysis.

The MT Box-C cryogenic separation system, interfaced directly to MAT252 mass spectrometer, uses a slightly different trapping procedure to that employed at INSTAAR. Sample air passes through two small-volume traps, maintained at −196°C, at a flow rate of about 5 ml/min. H_2O and CO_2 are trapped in the first of these two traps. After processing the required volume of air, the first of these two traps is heated to −100°C and the CO_2 is cryo-distilled into the second trap. The yield of CO_2 is then determined (for use by the automated analysis procedures) and a second cryo-distillation of the CO_2 into a micro-volume trap follows. The CO_2 is analyzed directly from this micro-volume. The entire inlet system is manufactured from stainless steel and all valves in the MT Box-C are constructed from stainless steel with gold seats. The MT Box-C device has a 12-port manifold to which 10 sample flasks and one or two air standards are connected for a typical analysis sequence. Sample flasks are connected to the MT Box-C using Cajon Ultra-Torr fittings fitted with Viton o-rings. Air standards are connected using Swagelok stainless steel fittings. Details of the MT Box-C are given in [15].

N_2O cannot be physically separated using the procedures employed at CSIRO and is co-trapped from air samples with CO_2. The procedure to correct for the presence of N_2O is described previously.

2.2.2 Mass spectrometers used at CSIRO

Between 1977 and 1991, a Micromass 602D dual inlet stable isotope ratio mass spectrometer was employed. In 1991, a Finnigan MAT252 dual inlet mass spectrometer was

commissioned and operated in parallel with the 602D for 18 months. Since 1992, the MAT252 has been used for all CO_2 isotopic analysis at CSIRO Atmospheric Research. The basic principles of operation of these mass spectrometers are similar to those described above for the INSTAAR mass spectrometer and are not detailed here.

At CSIRO, we have identified a number of systematic effects in the measurements of stable isotope ratios of CO_2. Two significant effects that are regularly monitored, and for which we have developed correction procedures, are termed the "bleed effect" and the "working gas effect". The bleed effect arises from the small depletion of $^{12}CO_2$, with respect to $^{13}CO_2$, in the reference CO_2 gas that occurs over time. We treat this effect in two ways. First, we replace the working gas in the bellows frequently to minimize the effect, and second, we quantify the magnitude of the effect and apply a correction to all measured samples based on the elapsed time between loading and use of the reference gas. The working gas effect is a "memory effect" (and is also known as cross contamination) where a small amount of sample gas is analyzed with the reference gas and a small amount of reference gas is analyzed with the reference gas. The result of this effect is to reduce the magnitude of the measured difference between sample and reference gas. Measuring this effect on CO_2 gases with significantly different isotopic composition from the reference gas monitors the effect and allows a correction procedure to be applied. These effects have been described in more detail elsewhere [1,12,24]. Modifications were made to the ion source of the MAT 252 in 1997 that reduced the working gas effect considerably.

2.2.3 Standards and calibrations

The $CO_2\delta^{13}C$ and $\delta^{18}O$ data are reported on the international VPDB-CO_2 scale. First, $\delta45$ and $\delta46$ values of sample CO_2 are obtained with respect to a pure reference CO_2. The reference CO_2 is one of 6 sub samples of an ultra-high purity high-pressure cylinder of CO_2 (HC453) maintained in large-volume glass containers. HC453 has been the sole source of reference CO_2 for use at CSIRO since 1977 and HC453 sub samples were measured against NBS-19 in the 1980's resulting in an assignment of VPDB-CO_2 values of $\delta^{13}C = -6.396‰$, and $\delta^{18}O = -13.176$ ‰ [17]. The link to VPDB-CO_2 has been maintained by comparisons between these sub-samples. Corrections to convert $\delta45$ and $\delta46$ values to preliminary $\delta^{13}C$ and $\delta^{18}O$ are applied using methods described by [4]. This includes correction for the presence of nitrous oxide, co-trapped with the CO_2, using measured concentrations of N_2O and CO_2 in each sample [15].

Final $\delta^{13}C$ and $\delta^{18}O$ values on the VPDB-CO_2 scale are obtained after a correction based on comparison of measured and assigned values in air standards (high-pressure cylinders of air) that are processed every 4 samples. The initial assignment of VPDB-CO_2 isotopic values to air standards was referred to as CG92 [2]. A revised assignment, CG99, was developed during 1999–2000, which takes into account recently identified and independently quantified systematic biases. The CG99 assignment is used here.

CSIRO expressions of the VPDB-CO_2 scale are monitored using a number of high-purity CO_2 standards (GS–19, GS-20, OZTECH-3, OZTECH-30, OZTECH-40) and a number of surveillance standards (high-pressure cylinders of air). The very small sample requirements mean that all high-pressure cylinder air standards used since 1991 remain in the surveillance suite. (Note: Measurements made on all surveillance gases are used solely for diagnostic, not adjustment, purposes).

CSIRO monitors its expression of the VPDB-CO_2 scale relative to those of other laboratories, using a range of samples that includes the three NIST high-purity CO_2 SRMs [30], the IAEA CLASSIC cylinders (two four-laboratory circulations of 5 cylinders) [5], flask

air sharing comparisons with several laboratories (for example, ~ six flasks of air per month with NOAA/CMDL since 1992) and through participation in other comparison exercises.

3. ISOTOPIC MEASUREMENTS USING GAS CHROMATOGRAPHY–ISOTOPE RATIO MASS SPECTROMETRY

3.1 Isotopic measurements at NIWA using GC-IRMS

The traditional method used to perform isotopic measurements of atmospheric CO2, dual-inlet IRMS, has the following two problems: 1) co-extraction and analysis of contaminating N_2O with the CO_2 of interest such that post-measurement correction is required and 2) the requirement for relatively large samples of CO_2 (a few tenths to several μmol) [11].

To avoid the problems and sources of error that arise due to this inclusion of N_2O in the CO_2 sample during dual-inlet analysis, either a standardized correction procedure must be used by all laboratories, as recommended by [4], or analysis of N_2O-free samples must be achieved.

To address these shortcomings in the dual inlet technique, a number of labs have been exploring the GC-IRMS technique (Gas Chromatography, Isotope Ratio Mass Spectrometry), which enables N_2O-free, high-precision isotopic analysis of atmospheric CO_2. Typically, GC-IRMS systems have significantly less precision than dual inlet techniques, and thus the primary challenge for GC-IRMS techniques is to achieve acceptable precision in the isotopic measurement. We describe here the system recently developed at NIWA in New Zealand [11].

3.2 Experimental setup at NIWA

3.2.1 GC-IRMS inlet system

The layout of the GC-IRMS system is shown in Figure 6. The basic components are as follows. A 10-port valve (Valco Instruments Co. Inc., Houston, Texas) is used to direct sample air into the GC, an HP5890 Series II (Hewlett Packard, Avondale, Pennsylvania, USA). Switching between sample/reference gases and vacuum on/off is performed with pneumatic valves (Nupro) controlled by LabView™ (National Instruments, Austin, Texas, USA). Sample aliquot introduction into an evacuated sample loop and pressure-equilibration-volume (PEV) before injection is described in section 3.2.3. Gas separation is performed with a packed column described in Section 3.3.1.

After GC separation, sample gas enters the open split interface via a Nafion™ MD — Series Gas Drier (Perma Pure Inc., Toms river, New Jersey,) which is discussed further in Section 3.3.2.1. Two independent air-actuated pistons switch between the sample capillary (deactivated quartz glass, 0.32 mm ID flow rate 3.0 ml/min) and the helium purge gas capillary (deactivated quartz glass, 0.32 mm ID flow rate 5 ml/min). Transfer of sample gas or purge helium from the open split to the IRMS was through a deactivated glass capillary, 0.11 mm ID, 1 m long, (SGE, International Pty Ltd., Ringwood, Victoria, Australia) at a flow rate of 0.3 ml/min. Obtainable precision is critically dependent on the open split design, which is further discussed in Section 3.3.2.2.

Isotopic analysis of CO_2 is performed by a Finnigan MAT 252 IRMS with an accelerating potential of 10 kV. This IRMS utilizes a Multielement — Multicollector (MEMCO) system with Faraday cups connected to feedback resistors of 3×10^8, 3×10^{10}, and 1×10^{11} Ω to simultaneously measure m/e 44, 45, and 46 ion currents, respectively. The IRMS was tuned for a compromise between maximum sensitivity (<1200 molecules/ion) and

minimum nonlinearity (<0.10 ‰/V for $\delta^{13}C$ and <0.15 ‰/V for $\delta^{18}O$, respectively) between ~0.2 and 1.5 V (~0.7 to 5 nA) m/e 44. In the course of the development, new Finnigan source slits were installed to the IRMS, the advantages of which are discussed in Section 3.3.1.

3.2.2 Analysis procedure

Routine analysis is provided by injection and analysis of (1) a reference gas aliquot, (2) three aliquots of a sample, and (3) a second aliquot of the same reference gas. The average 44/45 and 46/44 ratios and areas of the two reference gas aliquots are used to calculate $\delta^{13}C$, $\delta^{18}O$, and the CO_2 mixing ratio of the sample, respectively. This bracketing of the sample aliquots with reference gas aliquots further reduces the effect of any instrumental drift that may occur during the period of analysis.

During the analysis procedure the sample loop and adjacent plumbing (see Figure 6) are first purged with reference gas for 30 s at a flow rate of 60 ml/min. The flow is stopped, and pressure equilibrates for 5 s after which injection through both the precolumn and main column occurs for 230 s. Following injection, the precolumn is back flushed for 270 s. Meanwhile, the open split interface switches from directing pure helium to the IRMS to sample effluent, ~60 s before the eluting CO_2 peak. Integration of the CO_2 peak follows. Approximately 45 s after the final integration point of the CO_2 peak, the open split redirects the flow to the IRMS to pure helium.

For sample gas aliquots the sample loop and adjacent plumbing are evacuated rather than pressure flushed. To ensure peak reproducibility, the same amount of gas must be introduced to the IRMS for each sample aliquot. Thus each sample aliquot must be at the same pressure, volume, and temperature (PVT). To facilitate this, a vacuum is applied to the sample flask valve, through the 0.5 ml sample loop and into a 5 ml PEV, 1.36m × 3.175 mm OD (1.016 mm ID.). After introduction of the sample aliquot to the sample loop, the PEV valve is opened to enable sample loop equilibration to ambient pressure. For samples flasks with above ambient pressures, outflow from the PEV to the laboratory atmosphere occurs, and for samples at or below ambient pressure, inflow from the laboratory atmosphere into the PEV occurs. This equilibration is necessary to ensure that sample/reference gas injections are at the same PVT. During this equilibration for samples collected at or below ambient pressure, the PEV is necessary to avoid contamination by stopping "suck back" or inflow of laboratory air into the sample loop. Furthermore, during sample loop filling, up to 5 ml of sample gas purges through the sample loop to ensure that no residual from a previous sample or reference gas is injected as a contaminant.

Initially, for each new sample, the PEV valve is closed, and all plumbing to the flask valve is evacuated by a turbo molecular pump to a pressure of ~0.01 Pa. This volume is filled, re-evacuated, and refilled before an analysis commences. The vacuum pump connection then switches from turbo to roughing pump for the automated run. After the reference gas injection and 450 s prior to each subsequent sample injection, the PEV valve is closed, and the PEV, sample loop, and adjacent plumbing are evacuated. Typically, a vacuum of ~0.02 Pa is obtained in this time, after which the vacuum inlet is closed, and the sample valve opens, filling the sample loop, PEV, and adjacent plumbing. To ensure equilibration between the sample flask and sample loop, the sample valve remains open for 30 s. Pressure equilibration of each sample aliquot to ambient pressure then occurs by opening the PEV valve for 5 s. To avoid sample contamination during pressure equilibration of each sample aliquot, it is critical that inflow of laboratory air into the inlet volume must not pass beyond the PEV.

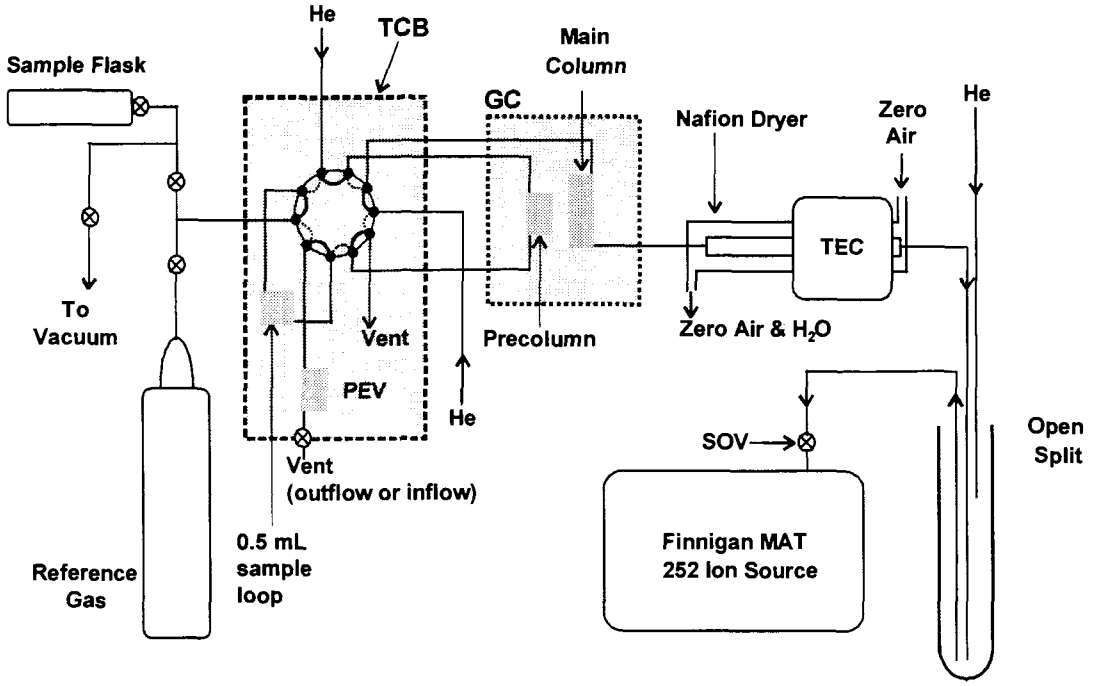

Figure 6. Gas chromatograph—isotope ratio mass spectrometry (GC-IRMS) schematic. The 10-port valve and adjacent plumbing are enclosed in a temperature controlled box (TCB) and automatically switch between load/back flush (solid loops) and inject (dashed loops). Pressure equilibration of sample gas before injection to the GC column occurs in the pressure-equilibration-volumn (PEV). After GC separation, gas effluent flows through a Nafion drier and enters the open split. The Nafion drier is cooled by a thermoelectric cooler (TEC) and is purged by a countercurrent flow of clean dry "zero" air. To enable gas stream switching, the sample and purge helium capillaries alternately move into the immediate proximity of the tip of the transfer capillary, which is permanently positioned at the bottom of the open split. The open split has two positions: (1) "open split in," (sample capillary extended and helium capillary retracted, as shown in figure1), where the Finnigan MAT 252 IRMS receives undiluted GC sample effluent and, (2) "open split out" (sample capillary retracted and helium capillary extended), where the Finnigan MAT 252 IRMS, receives pure helium. The shutoff valve (SOV) is closed to enable operation of the IRMS in dual-inlet mode.

For routine analysis (three aliquots) of air samples collected at ambient pressure, total sample usage is 45 ml. This usage is high compared with the total amount actually injected onto the column (three 0.5 ml aliquots) and is currently limited by the 15 ml inlet volume (sample loop, PEV, and adjacent volume). For routine analysis of an air sample collected to 100 kPa total sample usage is 90 ml. This higher total sample usage (compared to that required for air samples collected at ambient pressure) results because the 15 ml inlet volume is filled to the pressure at which the sample was collected (~100 kPa above ambient pressure), rather than ambient pressure.

3.3 Results and discussion of the GC-IRMS system

3.3.1 Separation of CO_2 and N_2O

Porapak-Q was found to provide the best separation between CO_2 and N_2O. After the installation of the new Finnigan memory effect reducing source slits, the excessive "tailing" of

the CO_2 peak was reduced, and the CO_2 — N_2O separation was improved. This made possible complete separation of N_2O from the integrated CO_2 peak (Figure 7) to enable N_2O-free determinations of $\delta^{13}C$ and $\delta^{18}O$ of atmospheric CO_2.

The specifics of the column used is a Porapak-Q, 3.66 m × 1.59 mm OD (1.016 mm ID), stainless steel, 80/100 mesh with a 1.83 m precolumn of the same material (Alltech). This is used at a temperature of 41°C with a helium carrier gas flow rate of 3.0 ml/min.

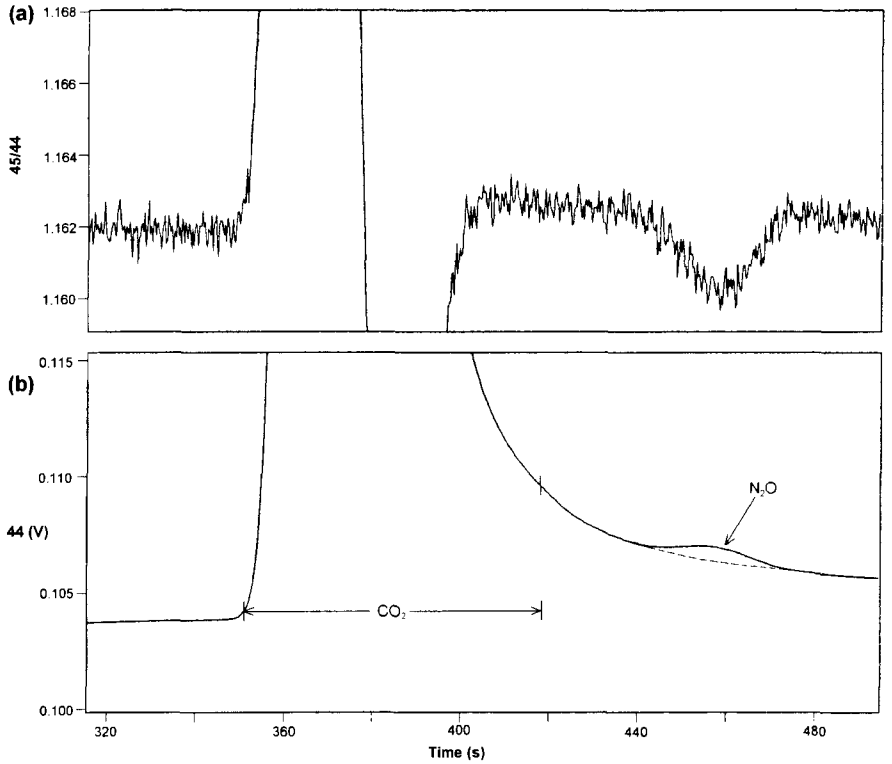

Figure 7. (a) 45/44 isotope ratio and (b) mass 44 chromatogram. Results of separation using the memory effect reducing source slits: The tick marks shown are the positions at which the software starts and ends the peak integration. The 1000 times smaller N_2O peak, which is visible as a small blip on the large CO_2 tail, is completely separated from the integrated CO_2 peak, allowing for a completely N_2O-free calculation of $\delta^{13}C$ and $\delta^{18}O$ in CO_2.

3.3.2 Maximization of signal-to-noise ratio

3.3.2.1 Contamination and carrier gas purity

High carrier gas purity is required to minimize background contamination and noise. This is achieved with the use of an in-line gas purifier (ALL-Pure Helium Purifier, Alltech) to purify helium of purity greater than 99.995% so that contaminants (CO, CO_2, O_2, H_2O, and NMHCs) were reduced to ppb levels.

Entrainment of laboratory air into the inlet system results in increased background levels and noise and loss of precision. This is mainly because laboratory air is relatively "wet," and the formation of HCO_2^+ molecules in the ion source contributes to a loss of precision and accuracy [22]. Thus it is imperative for high-precision results to maintain the inlet system completely leak free and dry. IRMS background water levels are minimized and

maintained at a constant level by passing all GC effluent through a Nafion drier consisting of a 610 mm long, 0.762 mm ID Nafion tubular membrane in a 1.59 mm OD stainless steel sheath. Clean, dry "zero" air (dew point < –80 °C) purges the Nafion drier at a flow rate of ~100 ml/min. The Nafion purge flow (~100 ml/min) is high compared to the sample flow (~3 ml/min) to ensure high drier performance [21]. A thermoelectric cooler (TEC) (Tropicool, Christchurch, New Zealand) cooled the second half of the Nafion to 0 °C. By cooling the Nafion the vapor pressure in equilibrium with the membrane decreases, and the effectiveness of the drying is enhanced [21]. The addition of the TEC decreases the dew point of the emerging dried gas from ~ –45°C to < –80°C, corresponding to a drop in background water (m/e 18), as measured on the most sensitive detector in the Finnigan MAT 252 IRMS, from 2.2 to 1.030 V (2.2 to 1.03 pA).

3.3.2.2 Open split design

The open split interface is an integral part of the system as it forms the critical GC-IRMS link and allows for the continuous flow of either sample gas or pure helium into the IRMS. For this application, the open split is designed to minimize entrainment, contamination, and sample dilution and maximize reproducibility and precision. The open split is a Pyrex glass test tube, open at the top, with the following dimensions: 60 mm long, 1.9 mm OD, and 1.3 mm ID. Gas stream switching, previously described in Figure 6, enables a high signal-to-noise ratio. The split ratio is ~1:9; that is, of the sample effluent that enters the open split at 3.0 ml/min, only ~10 % actually enters the ion source at 0.3 ml/min (this factor is currently limited by chromatography and not the open split design). Thus, in the technique described here and for samples at current atmospheric levels, ~8 nmol CO_2 is injected onto the GC column, and 0.8 nmol of this enters the IRMS source.

3.3.3 Reproducibility: temperature and pressure effects

Reproducibility and precision of the measured CO_2 mixing ratio are strongly affected by temperature and pressure variations that occur for each eluting peak during a GC-IRMS analysis. Because of the IRMS nonlinearity, $\delta^{18}O$ and $\delta^{13}C$ measurements are also affected.

Temperature variations are generally nonlinear and non-monotonic over the analysis period and are therefore important for reproducibility. In addition, temperature variations change the value of the high-precision resistor that regulates the magnet current in the Finnigan MAT 252 IRMS, (*W. Brand*, personal communication, 1999). The detected signals are therefore affected because magnetic field strength variations cause the ion beam to be shifted.

The background noise is further magnified when operating in GC-IRMS mode, owing to variations in open split entrainment. This occurs because the relative pressure difference between the slightly above ambient pressure open split (due to the purge helium) and the laboratory is affected by temperature variations. This further highlights the need for a well-designed open split so that minimal (if any) entrainment and IRMS contamination occurs.

The effects of laboratory temperature variations should be minimized by stabilizing the inlet system temperature to <0.2°C/h. Insulation of the inlet system, from the reference gas regulators through to the open split, can achieve this. In addition, temperatures are stabilized in the transfer capillary and SOV to the IRMS to <0.1°C/h by insulation of the section. Furthermore, the sample loop, PEV, and adjacent plumbing are maintained at a stable temperature of 35.00 ± 0.02°C by enclosing this section within an insulated, temperature-controlled box (TCB). Temperature control to this level within the TCB is achieved with the

use of an external GC temperature sensor and a 40 W cartridge heater. A 2 W electric fan circulated air within the box, and two thermal masses of 150 ml water and 1.6 kg brass were positioned in the box. These measures reduced the uncontrollable temperature effects due to laboratory air temperature variations and improved technique precision.

3.3.4 Analysis time

The analysis time is determined by the requirements for sufficient N_2O–CO_2 separation, high signal-to-noise ratio, and a sufficient number of reference and sample aliquots for good statistics and to reduce instrumental drifts. The analysis time includes the time required for extraction of CO_2 from the air sample. Increasing the carrier flow rate in the column decreases the analysis time. However, reduced separation and increased sample dilution occurs, resulting in lowered signal strength, reduced signal-to-noise ratio, and lowered precision. A balance between the analysis time, adequate separation, dilution, and precision is achieved at an analysis time of 40 min, which is comparable to that required for dual-inlet analysis.

Using the technique described here, mass spectrometers that have a large memory effect may not be used (without modification) to obtain high-precision, N_2O-free isotopic analyses of atmospheric CO_2 in short analysis times.

3.3.5 Technique performance

Maximum performance can be evaluated by considering the "shot noise limit." This limit is based on ion collection statistics and refers to the precision that would be obtained if the ion beam were the only significant noise source [27]. Simplified expressions from [25] for the shot noise limited precision (σ_δ) expressed as functions of the integrated m/e 44 signal area (^{44}A, V·s) are

$$\sigma_\delta^2 = 0.00892/^{44}A$$

If the integrated ion currents of the reference and sample are not equal, then

$$\sigma_\delta^2 = 0.00446(1/^{44}A_{\text{reference}} + 1/^{44}A_{\text{sample}})$$

In the initial paper describing this technique by [11] the precision of the technique for $\delta^{13}C$, $\delta^{18}O$, and CO_2 mixing ratio, determined by both analysis of atmospheric air samples and replicate analyses of air standards, was 0.02 ‰, 0.04‰ and 0.4 ppm, respectively. Comparing the observed and theoretical shot noise limited $\delta^{13}C$ precision, it was seen that the technique performs at the shot noise limit of 0.02‰.

Evaluating technique performance over a range of sample sizes can be performed by introducing differing amounts of CO_2 to the ion source of the IRMS by varying the open split dilution. The split ratio of 1:9 was increased by introducing reference and sample CO_2 with the helium capillary also extended and increasing the open split helium purge flow from the normal 5 ml/min to ~20 ml/min. Replicate analyses of an air standard by this method are shown in Figure 8. Over the observed range of 150 pmol to 1 nmol CO_2 in the source, the technique performs within a factor of 1.3 of the shot noise limit. At the lower limit of 150 pmol CO_2 in the source, the technique performs within a factor of 1.5 from the shot noise limit, indicating that the effects of noise or systematic error become more significant at these lower sample sizes.

It can be seen from the theoretical prediction (Figure 8) that by increasing the amount of gas reaching the IRMS source (while maintaining matched reference and sample sizes), higher performance (i.e. lower standard deviation) is possible. However, this performance is ultimately limited by IRMS detector overload, which for eluting CO_2 peaks from the experimental technique presented here in a Finnigan MAT 252 IRMS, would occur at ~4 nmol CO_2 in the source. A shot noise limited precision of 0.01‰ is theoretically possible with 3 nmol CO_2 in the source. This would be possible by this technique if the split ratio could be reduced to ~1:2.2. This precision is comparable to that of the dual inlet technique.

While this theoretical precision has yet to be achieved on a routine basis, GC-IRMS measurements, even at a coarser precision, opens many new doors for analysis of isotopes in atmospheric CO2. These new opportunities for trace gas research are now possible because of the smaller sample requirement of GC-IRMS. The logistics of new sampling methods (e.g. sampling from pilot less aircraft (kites and gliders) and international commercial flights) will be eased as will sampling and analyzing CO_2 from ice cores. Traditionally, large volumes of carbon-containing trace gases are converted off-line to CO_2 for $\delta^{13}C$ analysis, for example, up to 35 L for CH_4 [23]. The GC-IRMS technique developed in this work can be used as a "front end" in a modular approach to GC-IRMS for other carbon-containing trace gases. On-line preparation of trace amounts of gases can be performed by miniaturized versions of existing methods and injected directly into the CO_2 GC-IRMS system presented here for isotopic and mixing ratio analysis.

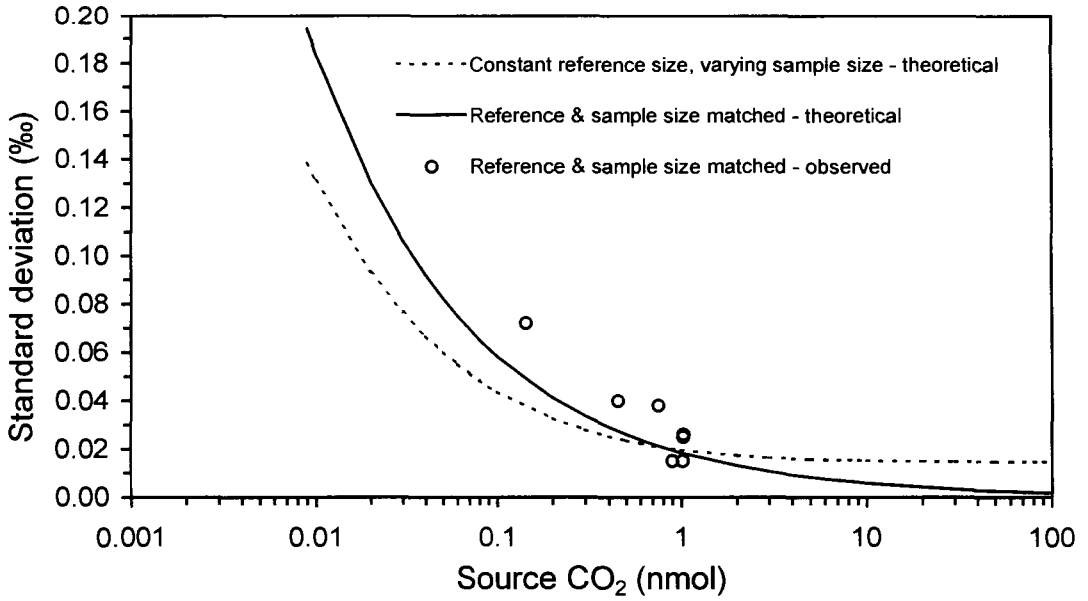

Figure 8. Observed and theoretical (shot noise limited) standard deviations for varying amounts of CO_2 in the IRMS source.

4. CONCLUSIONS

Isotopes in atmospheric CO_2 are key properties for separating terrestrial biospheric and oceanic exchanges of carbon with the atmosphere and for potentially separating regional scale respiratory and photosynthetic fluxes in terrestrial ecosystems. The primary challenge is to achieve acceptable accuracy and precision and to maintain them over the decades needed to

observe variability of the carbon cycle. We are pushing our analytical capabilities to their limit in this application of stable isotopes, and small artifacts that may be unobservable or unimportant in normal mass spectrometry will become important.

The keys to success in this approach are diligent intercalibrations of laboratories from around the world, as well as the use of multiple techniques such as dual inlet and GC-IRMS mass spectrometery.

REFERENCES

[1] ALLISON, C.E., FRANCEY, R.J., High precision stable isotope measurements of atmospheric trace gases, in Reference and Intercomparison Materials for Stable Isotopes of Light Elements, pp. 131–153, Int. At. Energy Agency, Vienna, 1995.

[2] ALLISON, C.E., FRANCEY, R.J. $\delta^{13}C$ of atmospheric CO_2 at Cape Grim: The in situ record, the flask record, air standards and the CG92 calibration scale, in Baseline Atmospheric Program Australia *1999*, edited by A.L. Dick, N.A. Derek, and W. Bouma, pp. 45–56 Bureau of Meteorology, Melbourne, Victoria, Australia.

[3] ALLISON, C.E., FRANCEY, R.J. (in preparation), Calibration of stable isotope measurements of atmospheric CO_2 at CSIRO Atmospheric Research.

[4] ALLISON, C.E., FRANCEY, R.J., MEIJER, H.A.J. Recommendations for the reporting of stable isotope measurements of carbon and oxygen in CO_2 gas, in Reference and Intercomparison Materials for Stable Isotopes of Light Elements, pp. 155–162, Int. At. Energy Agency, Vienna, 1995.

[5] ALLISON, C. E., FRANCEY, R. J., STEELE, L. P. The International Atomic Energy Agency Circulation of Laboratory Air Standards for Stable Isotope Comparisons: Aims, preparation and preliminary results, IAEA, Vienna.

[6] CIAIS, P., TANS, P., WHITE, J.W., FRANCEY, R., TROLIER, M., BERRY, J., RANDALL, D., SELLERS, P., COLLATZ, J., SCHIMMEL, D. (1995). The global carbon budget inferred from a new worldwide data set of $\delta^{13}C$ measurements in atmospheric CO_2. J. Geophys. Res, 100 D3, 5051–5070.

[7] CIAIS, P., DENNING, A.S., TANS, P.P., BERRY, J.A., RANDALL, D.A., COLLATZ G.J., SELLERS, P.J., WHITE, J.W.C., TROLIER, M., MEIJER, H.A.J., FRANCEY, R.J., MONFRAY, P., HEIMANN, M. (1997). A three-dimensional synthesis study of $\delta^{18}O$ in atmospheric CO_2. 1. Surface fluxes. J. Geophys. Res., 102, 5857–5872.

[8] MASARIE, ET AL., in preparation.

[9] COPLEN, T, B, Reporting of stable carbon, hydrogen, and oxygen isotopic abundances, in Reference and intercomparison materials for stable isotopes of light elements, 31–34, IAEA-TECDOC-825, Vienna, 1995.

[10] FARQUHAR, G.D., LLOYD, J., TAYLOR, J.A., FLANAGAN, L.B., SYVERTSEN, J.P., HUBRICK, K.T., WONG, S.C., EHLERINGER, J.R. (1993) Vegetation effects on the isotope composition of oxygen in atmospheric CO_2. Nature 363, 439–443.

[11] FERRETTI, D.F., LOWE, D.C., MARTIN, R.J., BRAILSFORD, G.B., A new gas chromatograph-isotope ratio mass spectrometery technique for high precision, N_2O-free analysis of $\delta^{13}C$ and $\delta^{18}O$ in atmospheric CO_2 from small air samples, Journal of Geophysical Research, Vol. 105, No. D5, p. 6709–6718, 2000.

[12] FRANCEY, R.J., ALLISON, C.E., (1995). "The trend in atmospheric $\delta^{13}CO_2$ over the last decade", Final Meeting of the Coordinated Research Programme on Isotope Variations of Carbon Dioxide and Other Trace Gases in the Atmosphere, Ed. K. Rozanski, Internal Report, IAEA, Vienna, 7–10 November 1994.

[13] FRANCEY, R.J., ALLISON, C.E., STEELE, L.P., LANGENFELDS, R.L., WELCH, E.D., WHITE, J.W.C., TROLIER, M., TANS, P.P., MASARIE, K.A. (1994). Intercomparison of Stable Isotope Measurements of CO_2, in Climate Monitoring and Diagnostics Laboratory CMDL No. 22 Summary Report 1993, edited by J.T. Peterson and R.M. Rosson, US Department of Commerce, NOAA, Boulder, Colorado, pp 106–110.

[14] GEMERY et al., 1993.

[15] FRANCEY, R.J., STEELE, L.P., LANGENFELDS, R.L., LUCARELLI, M., ALLISON, C.E., BEARDSMORE, D.J., CORAM, S.A., DEREK, N., DE SILVA, F., ETHERIDGE, D.M., FRASER, P.J., HENRY, R.J., TURNER, B.T., WELCH, E.D. (1996). Global Atmospheric Sampling Laboratory (GASLAB): supporting and extending the Cape Grim trace gas programs, Baseline Atmospheric Program (Australia) 1993. (eds. R.J.Francey, A.L.Dick and N.Derek) Bureau of Meteorology and CSIRO Division of Atmospheric Research, Melbourne, pp 8–29.

[16] FRANCEY, R.J. P. P. TANS (1987). The latitudinal variation in oxygen-18 of atmospheric CO_2. Nature 327: 495–497.

[17] FRANCEY, R.J., GOODMAN, H.S. (1988). The DAR stable isotope reference scale for CO_2. Baseline Atmospheric Program (Australia) 1986. (Eds. B.W. Forgan and P.J. Fraser). Department of Science/Bureau of Meteorology with CSIRO/Division of Atmospheric Research, Australia. p 40–46.

[18] FRANCEY, R.J., P. TANS, C.E. ALLISON, I.G. ENTING, J.W.C. WHITE, M. TROLLIER, Changes in oceanic and terrestrial carbon uptake since 1982, Nature, 373, 326–330, 1995.

[19] KEELING, C.D., BACASTOW, R.B., CARTER, A.F., PIPER, S.C. WHORF, T.P., HEIMANN, M., MOOK, W.G. ROELOFFZEN, H. (1989). A three-dimensional model of atmospheric CO_2 transport based on observed winds: 1. Analysis of observational data. Geophysical Monograph 55, Aspects of Climate Variability in the Pacific and the Western Americas (Ed. David H. Peterson), American Geophysical Union, pp 165–236.

[20] KEELING, C.D., WHORF, T.P., WAHLEN, M., VAN DER PLICHT, J. (1995). Interannual extremes in the rate of rise of atmospheric carbon dioxide since 1980. Nature 375, 666–670.

[21] LECKRONE, K.J., J.M. HAYES, Efficiency and temperature dependence of water removal by membrane dryers, Anal. Chem., **69**, 911–918, 1997.

[22] LECKRONE, K.J., J.M. HAYES, Water-induced errors in continuous-flow carbon isotope ratio mass spectrometery, Anal. Chem., 70, 2737–2744, 1998.

[23] LOWE, D.C., M.R. MANNING, T. BROMLEY, W. ALLEN, G. BRAILSFORD, D. FERRETTI, A. GOMEZ, R. KNOBBEN, R. MARTIN, M. ZHU, R. MOSS, Shipboard determinations of the distribution of $\delta^{13}C$ in atmospheric methane in the Pacific, J. Geophys. Res., 104, 26, 125–26, 135, 1999.

[24] MEIJER, H.A.J., NEUBERT, R.E.M., VISSER, G.H. (2000), Cross contamination in dual inlet isotope ratio mass spectrometers. International Journal Of Mass Spectrometry 198(1–2), 45–61.

[25] MERRITT, D. A., J. M. HAYES, Factors controlling precision and accuracy in isotope-ratio-monitoring mass spectrometry, Anal. Chem., 66, 2336–2347, 1994.

[26] NAKAZAWA, T., MORIMOTO, S., AOKI, S., TANAKA, M., (1997). Temporal and spatial variations of the carbon isotopic ratio of atmospheric carbon dioxide in the western Pacific region, J. Geophys. Res. - Atm, 102, 1271–1285.

[27] PETTERSON, D.W., J.M. HAYES, Contempory Topics in Analytical and Clinical Chemistry, pp. 217–252, Plenum, New York, 1978.

[28] TANS, P.P., BERRY, J.A., KEELING, R.F. (1993). Oceanic $^{13}C/^{12}C$ observations: A new window on ocean CO_2 uptake. Global Biogeochemical Cycles 7, 353–368.

[29] TANS, P.P., FUNG, I.Y., TAKAHASHI T. (1990). Observational constraints on the global atmospheric carbon dioxide budget. Science 247, 1431–1438.

[30] VERKOUTEREN, R.M. (1999). Preparation, Characterization, and Value Assignment of Carbon Dioxide Isotopic Reference Materials: RMs 8562, 8563, and 8564. Anal. Chem.71, 4740–4746.