



# THE INTERNATIONAL ATOMIC ENERGY AGENCY CIRCULATION OF LABORATORY AIR STANDARDS FOR STABLE ISOTOPE COMPARISONS: AIMS, PREPARATION AND PRELIMINARY RESULTS

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**Abstract.** Ten air standards in high-pressure aluminium cylinders were prepared, covering a specified range of CO<sub>2</sub> concentration and δ<sup>13</sup>C and δ<sup>18</sup>O isotopic composition, to be used for laboratory intercomparisons with the primary aim of merging global atmospheric CO<sub>2</sub> δ<sup>13</sup>C data sets. After establishing the stability of the standards, five were circulated between four laboratories with established high precision global monitoring networks to quantify differences between the measurement scales used in the laboratories. Measurements of CO<sub>2</sub> concentration in three of the four laboratories showed agreement to better than 0.2 ppm for the five standards. Measurements of N<sub>2</sub>O concentration reported by three of the laboratories agreed to better than 3 ppb after correction for known scaling factor differences, but a fourth laboratory reported results for two cylinders lower by about 20 ppb, contributing a δ<sup>13</sup>C uncertainty of about 0.012 ‰ for these two cylinders. The reported measurements of the δ<sup>13</sup>C and δ<sup>18</sup>O of CO<sub>2</sub> extracted from the air in the five standards showed large offsets between the laboratories of up to 0.1‰ in δ<sup>13</sup>C and up to 1‰ in δ<sup>18</sup>O. Analysis of the results shows that about 40% of the offsets arises from differences in the procedures used in each laboratory to calculate the δ<sup>13</sup>C and δ<sup>18</sup>O values from the raw measurements and that the remainder arises from the pre-concentration step. Using one of the circulated standards to "normalise" the others removes most of the inter-laboratory differences but there remains a non-linear response in one or more laboratories. The differences in δ<sup>13</sup>C that remain after normalisation are larger than the target precision of 0.01 ‰.

## 1. INTRODUCTION

Measurements of the concentration and isotopic composition of CO<sub>2</sub> in the atmosphere play a key role in understanding the global carbon budget. Several sample collection networks provide spatial and temporal coverage of CO<sub>2</sub> concentration and its stable carbon (δ<sup>13</sup>C) and oxygen (δ<sup>18</sup>O) isotopic composition [1,2,3,4]. However, there are problems in comparing the collected data to the target precision specified for budgeting studies [5] of 0.05 ppm for CO<sub>2</sub> concentration and 0.01‰ (per mil) for δ<sup>13</sup>C<sup>1</sup> (no specific precision target for δ<sup>18</sup>O has yet been recommended in this forum). For CO<sub>2</sub> concentration, the target precision is close to the internal analytical precision that is routinely obtained by most laboratories. In the most recent international World Meteorological Organization (WMO) round-robin exercise [7], eighteen laboratories measured air in sets of three high-pressure cylinders that had been analysed by one central laboratory to have CO<sub>2</sub> concentrations of about 342 ppm, 360 ppm

<sup>1</sup> The δ-notation is used for stable isotope composition. This notation expresses the ratio of the abundance of the heavy isotope to the abundance of the light isotope in a sample, eg <sup>13</sup>C and <sup>12</sup>C in CO<sub>2</sub>, with respect to the same ratio in a reference material as

$$\delta^{13}\text{C} = \frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{Sample}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{Reference}}} - 1.$$

As δ<sup>13</sup>C values are very small, they are usually multiplied by 1000 and given the units "per mil" or "‰". For CO<sub>2</sub> the Reference is VPDB-CO<sub>2</sub> (realised through the preparation of NBS19 carbonate) and is usually identified by δ<sup>13</sup>C<sub>VPDB</sub> (see [6] for more details). Throughout this paper, δ<sup>13</sup>C and δ<sup>18</sup>O are used to refer to isotope measurements in general and for explicit values. Where explicit values are used, the VPDB-CO<sub>2</sub> standard is assumed.

and 375 ppm. Of the eighteen laboratories, only eight, six and four agreed with the central laboratory to within 0.05 ppm at these CO<sub>2</sub> concentrations respectively. GLOBALVIEW-CO<sub>2</sub> [8] is a pioneering attempt to merge CO<sub>2</sub> concentration data from many international laboratories; however, the GLOBALVIEW-CO<sub>2</sub> compilation generally does not yet incorporate intercalibration differences such as those observed in the WMO comparison. For the isotopes of atmospheric CO<sub>2</sub>, merging data from different laboratories is even less advanced.

To address this, the International Atomic Energy Agency (IAEA) Isotope Hydrology Section established a project inside their Co-ordinated Research Project on Isotope Aided Studies of Atmospheric Carbon Dioxide and Other Trace Gases — Phase II, to produce and test a set of high-pressure air standards for interlaboratory comparisons. This project is known as CLASSIC: Circulation of Laboratory Air Standards for Stable Isotope inter Comparisons [9].

The initial CLASSIC proposal was for CSIRO Atmospheric Research to prepare ten air standards: high-pressure cylinders of air with CO<sub>2</sub> concentration and isotopic composition bracketing that of the present atmosphere. The composition of the air in the standards was designed so that CO<sub>2</sub> concentration ranged from about 320 ppm to 400 ppm,  $\delta^{13}\text{C}$  ranged from about -6‰ to -10‰ and  $\delta^{18}\text{O}$  varied from about 0‰ to -4‰. The co-variation of  $\delta^{13}\text{C}$  with CO<sub>2</sub> was selected to be similar to that observed in CO<sub>2</sub> exchange between the atmosphere and the terrestrial biosphere. Further, it was planned to vary the concentration of nitrous oxide (N<sub>2</sub>O) in the standards to test the procedure used to correct for N<sub>2</sub>O (co-trapped with the CO<sub>2</sub> in the cryogenic extraction procedures used in all four laboratories) that interferes with the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  measurements. To this end, the ten standards were prepared as two sets of five: each set of five covering the target CO<sub>2</sub> concentration and isotopic composition ranges but one set having elevated N<sub>2</sub>O concentrations. Five standards were selected for circulation from the ten prepared. Sample handling and data reporting protocols were prepared and distributed with the standards (see Section 2.3). These protocols were designed to minimise uncertainties that may arise from sample handling procedures and to elucidate uncertainties that may arise from CO<sub>2</sub> extraction from air, ion correction algorithms (<sup>17</sup>O, N<sub>2</sub>O) and mass spectrometer non-linearity [10, 6].

In order to make a preliminary assessment of the feasibility and effectiveness of intercalibrating stable isotope measurements with air standards in high-pressure cylinders, four laboratories with established measurement programs were selected. The four laboratories are identified in Table 1 [CSIRO:11, CMDL:4, SIO:12, TU:3]. Each of these four laboratories possess methodologies for high-precision measurement of the concentration of CO<sub>2</sub> and N<sub>2</sub>O in addition to their ability to perform high-precision isotopic composition measurements on CO<sub>2</sub> extracted from atmospheric air. Table 1 summarizes the techniques used in each of the laboratories. Assessment of the results occurred after a complete circulation of the subset of five standards that started and finished with analysis at CSIRO.

Along with the CLASSIC standards, two low-pressure canisters of high purity CO<sub>2</sub> with isotopic composition close to that of atmospheric CO<sub>2</sub> were circulated between the four laboratories to provide isotopic measurements free from any effects that may arise from the pre-concentration step, i.e. the extraction of CO<sub>2</sub> from air. These canisters of CO<sub>2</sub>, designated GS19B and GS20B, were provided by the University of Groningen [13]. The IAEA has provided a set of international reference materials, comprising NBS19 and NBS18 carbonates and VSMOW and SLAP waters, to each laboratory, independently of the gases, to use for calibration purposes. This first report describes the preparation of the ten air standards and presents the results from the first completed circulation of the five CLASSIC standards and the two low-pressure canisters of CO<sub>2</sub>.

**Table 1. Details of the laboratories involved in the initial circulation of the classic standards. For each species, the technique used in each laboratory, and the typical volume of air (at STP) required for the analysis of that species, is given.**

Laboratory	Commonwealth Scientific and Industrial Research Organisation - Atmospheric Research, Aspendale, Victoria, Australia	Institute of Arctic and Alpine Research, University of Colorado, Boulder, Colorado, USA & National Oceanic and Atmospheric Administration Climate Monitoring & Diagnostics Laboratory, Boulder, Colorado, USA	Scripps Institution of Oceanography, University of California, San Diego, California, USA	Center for Atmospheric and Oceanic Studies, Tohoku University, Sendai, Japan
Code	CSIRO	CMDL	SIO	TU
Contacts	C.E. Allison & R.J. Francey	J.W.C. White & P.P. Tans	M. Wahlen	T. Nakazawa
CO <sub>2</sub>	GC-FID <sup>1</sup> 30 millilitres	NDIR <sup>2</sup> 200 millilitres	NDIR n/a	NDIR 900 millilitres
N <sub>2</sub> O	GC-ECD <sup>3</sup> 30 millilitres	GC-ECD n/a	GC-ECD 500 millilitres	GC-ECD 150 millilitres
δ <sup>13</sup> C & δ <sup>18</sup> O	Dual Inlet IRMS <sup>4</sup> (Finnigan MAT252) Online extraction 50 millilitres	Dual Inlet IRMS (Fisons OPTIMA) Online extraction 400 millilitres	Dual Inlet IRMS (Fisons PRISM II) Offline extraction 5 litres	Dual Inlet IRMS (Finnigan DELTA S) Offline extraction 500 millilitres

<sup>1</sup> GC-FID: Gas Chromatograph - Flame Ionisation Detector

<sup>2</sup> NDIR: Non-Dispersive Infra-Red analyser

<sup>3</sup> GC-ECD: Gas Chromatograph - Electron Capture Detector

<sup>4</sup> IRMS: Isotope Ratio Mass Spectrometer

## 2. THE CLASSIC STANDARDS

### 2.1 Filling of the cylinders

Ten 29.5 litre aluminium cylinders, manufactured by Luxfer (Riverside, California, USA) were purchased from Scott-Marin (Riverside, California, USA). Each cylinder is fitted with a Ceodeux brass, packless diaphragm valve and is used with a dedicated Air Products (Allentown, Pennsylvania, USA) nickel-plated brass body, 2-stage, stainless steel diaphragm regulator. Scott Specialty Gases, Inc. (San Bernadino, California, USA) passivated the internal cylinder surfaces using their ACULIFE IV process and filled the cylinders with clean dry nitrogen for shipping to CSIRO. After receipt at CSIRO each cylinder was vented and then flushed with chemically dried air following a procedure developed for archiving air [14, 15]. In the flushing procedure, each cylinder was pressurised to about 1100 kPa and vented to atmospheric pressure four times before being filled to about 6800 kPa. The cylinders were then vented and re-pressurised to 6800 kPa and stored for between seven and twenty-eight days prior to filling, as described below.

The flushing and filling of the cylinders was done at Cape Schanck on the southern coast of Australia (38°29'S, 144°53'E). Air was collected under conditions of strong, south westerly winds from the ocean using a high-pressure compressor system built around a RIX SA-3 "Sweet Air" oil-free compressor (RIX, Emeryville, California, USA). Two drying towers, each containing about 40 g of phosphorous pentoxide, were used to chemically dry the

air during collection. Each cylinder contained a mixture of about 3200 standard litres of dry air, 800 standard litres of "CO<sub>2</sub>-free" dry air (prepared by inserting a soda asbestos trap in series with the drying towers) and a few hundred millilitres of "spiking" CO<sub>2</sub> with a specific isotopic composition. Measurements of the water vapour levels in each of the standards with a Meeco Aquamatic + Moisture Analyser (Meeco, Inc., Warrington, Pennsylvania, USA) confirmed that in all cases the air standards contained water levels less than 1 ppm.

Five distinct spiking CO<sub>2</sub> gases were prepared by mixing two pure CO<sub>2</sub> gases with different isotopic compositions: one with  $\delta^{13}\text{C} = -28.5\text{‰}$  and  $\delta^{18}\text{O} = -19.5\text{‰}$  and the second with  $\delta^{13}\text{C} = 2.27\text{‰}$  and  $\delta^{18}\text{O} = 0.60\text{‰}$ . Two "spikes" of each target isotopic composition were prepared and a small amount of N<sub>2</sub>O (99%: Matheson Gas Products, East Rutherford, New Jersey, USA) was added to one of each pair. The compositions of the "spikes" are presented in Table 2.

**Table 2. Composition of the CO<sub>2</sub> AND N<sub>2</sub>O "spikes" added to the classic cylinders. The volumes, the  $\delta^{13}\text{C}$  and the  $\delta^{18}\text{O}$  values are nominal.**

CYLINDER	Volume of CO <sub>2</sub> Added (ml)	$\delta^{13}\text{C}$ ‰	$\delta^{18}\text{O}$ ‰	Volume of N <sub>2</sub> O added (μl)
CA01648	0	-	-	0
CA01609	160	2.27	0.60	0
CA01631	230	-7.09	-5.52	0
CA01672	300	-12.09	-8.78	0
CA01608	370	-15.19	-10.81	0
CA01632	440	-17.31	-12.19	0
CA01664	160	2.27	0.60	400
CA01691	230	-7.09	-5.52	400
CA01638	300	-12.09	-8.78	160
CA01660	370	-15.19	-10.81	400
CA01685	440	-17.31	-12.19	400

The CO<sub>2</sub> spikes were transferred, using liquid nitrogen, into a 300 ml stainless steel cylinder (Whitey Co., Highland Heights, Ohio, USA), fitted with two high-pressure valves (Autoclave Engineers, Erie, Pennsylvania, USA). This cylinder was inserted into the high-pressure stream of the compressor system and the contents flushed into the target cylinder with about 200 litres of dry air. The variation of  $\delta^{13}\text{C}$  with CO<sub>2</sub> concentration, from standard to standard, was designed to be -0.05 ‰ per ppm, similar to that observed for CO<sub>2</sub> exchange between the atmosphere and C-3 plants [16]. A specific  $\delta^{18}\text{O}$  variation with CO<sub>2</sub> concentration was not attempted. One extra cylinder, CA01648, an ACULIFE treated cylinder also, was filled with un-modified dry air from the sampling site for reference purposes. After filling, each cylinder was transported to CSIRO, fitted with a dedicated regulator and allowed to equilibrate for about 7 days before the water vapour content, trace gas concentrations and the carbon and oxygen isotopic composition of the CO<sub>2</sub> were measured. The analytical procedures used for the analyses have been described elsewhere [11, 17].

## 2.2 Logistic problems associated with circulating the cylinders

There are a number of problems associated with circulating high-pressure cylinders between laboratories. One is the cost of shipping, which is unavoidable, but needs to be addressed in future exercises to spread the shipping costs equally amongst the participating laboratories. Also, high-pressure cylinders are classified as dangerous goods and must be shipped with the regulator removed from the cylinder, introducing a further procedure that could affect the measurements when the regulators are removed and re-attached.

Instrumental problems were the major source of circulation delays during the first CLASSIC circulation. Two laboratories had lengthy delays due to instrument breakdowns and laboratory relocations. In total, the first circulation took nearly twenty months, almost twice as long as initially anticipated. It is expected that the second circulation of the CLASSIC standards (see below) will proceed much faster.

An unexpected, and serious, problem occurred involving a leak that developed across the main canister valve of GS19B. This resulted in the CO<sub>2</sub> becoming contaminated with air after only two laboratories had analysed the CO<sub>2</sub>. Inability to measure this sample has compromised the planned comparison of isotope measurements, in each laboratory, using CO<sub>2</sub> samples obtained independently of the pre-concentration steps.

## 2.3 Protocols

A set of protocols for sampling and reporting results was distributed with the standards to ensure consistent treatment at each laboratory. The protocols recommended:

As soon as possible after arrival, the cylinders are stored at the laboratory temperature to acclimatise.

- As soon as possible, the regulator and laboratory-supplied transfer-line are fitted to the cylinder. The regulator and transfer-line should then be pressurised and leak-tested.
- After leak-testing, the regulator delivery pressure is set to 10 psig and the transfer-line flushed and then capped. The cylinder valve is then opened to pressurise the regulator to full cylinder pressure and then closed. (The effectiveness of the maintenance of this pressure can be used as a confirmatory leak test).
- The regulator and transfer line are vented to atmospheric pressure and then re-pressurised three times every day for one week before the first analysis.
- All analytical techniques used and details of the relevant calibration scales are to be reported.
- Raw  $\delta_{45}$  and  $\delta_{46}$  values<sup>2</sup> are reported against the laboratory working gas (CO<sub>2</sub> in the reference variable volume).
- Assigned  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values for each CLASSIC standard are reported, including full corrections, and, if applicable, details of calibration of the measurements against working air standards.

Reporting sheets were provided to facilitate compliance with the protocols.

## 2.4 Circulation of the standards

The five circulating CLASSIC standards were analysed at CSIRO on several occasions between filling in 1995 and December 1996 when they were shipped to CMDL. The standards

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<sup>2</sup>  $\delta_{45}$  and  $\delta_{46}$  are the measured quantities before conversion to  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . For a more complete description see [6].

were analysed at CMDL in April 1997 and then shipped to SIO. The standards were analysed at SIO in December 1997 and then shipped to TU in early 1998. The standards were analysed at TU in May 1998 and returned to CSIRO where they were re-analysed in August 1998.

## 2.5 Measurement scales

This work does not establish a unique calibration scale, nor does it clarify the relationship between any one laboratory and an international calibration scale; however, some information on individual laboratory measurement scales is presented as background. In the detailed laboratory intercomparisons, the information provided by individual laboratories on their link to international calibration scales is not used.

CSIRO and CMDL report CO<sub>2</sub> concentration (mixing ratio) using the WMO X93 scale and TU use a scale based on gravimetrically prepared standards that is very close to the WMO X93 scale. Previous measurements by CSIRO, CMDL and TU using high-pressure cylinders of air have shown that CO<sub>2</sub> measurements made on these scales agree to within  $\pm 0.04$  ppm at ambient CO<sub>2</sub> levels (360 ppm). Details of the CO<sub>2</sub> measurement scale used at SIO were not reported.

CSIRO measurements of N<sub>2</sub>O concentration are based on the CMDL measurement scale with an observed scale factor of 0.9986 (CMDL/CSIRO) that produces agreement to about 0.4 ppb at current ambient levels (about 313 ppb). A scaling factor between CSIRO and SIO of 0.99252 (SIO/CSIRO) has also been established previously. No details of the N<sub>2</sub>O measurement scale used at TU were reported.

All laboratories report measurements of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  using the international VPDB-CO<sub>2</sub> scale [6].

## 3. RESULTS

### 3.1 Stability of the standards

#### 3.1.1 Initial analyses

The eleven standards were analysed soon after filling and occasionally until November 1996 when all standards were analysed prior to the five selected standards being despatched. Table 3 presents the average concentration for all species (except H<sub>2</sub>O and H<sub>2</sub>) and the CO<sub>2</sub> isotopic composition during the analysis period. The H<sub>2</sub>O content was measured only once, shortly after filling. For H<sub>2</sub>, the initial measured concentration in each cylinder is given and the quantity in parentheses is the annual increase of H<sub>2</sub> in that cylinder. These large, variable growth rates of H<sub>2</sub> have been observed in other ACULIFE treated cylinders used at CSIRO, but they have not been associated with storage problems for CO<sub>2</sub> and its isotopic composition [18].

The analyses show that the targets for trace gas concentration and CO<sub>2</sub> isotopic composition were achieved. The variation of  $\delta^{13}\text{C}$  with CO<sub>2</sub> concentration is about -0.05 ‰ per ppm, as planned, and the variation of  $\delta^{18}\text{O}$  with CO<sub>2</sub> concentration is about -0.04 ‰ per ppm. Also given in Table 3 are the usual precision limits for the analytical techniques used at CSIRO and the target precision for  $\delta^{13}\text{C}$  and CO<sub>2</sub>. From these results we consider the air in the cylinders to be stable for CO<sub>2</sub> and  $\delta^{13}\text{C}$ .

**Table 3. Results of the analysis by CSIRO of the ten prepared cylinders, and the cylinder of dried, natural Cape Schanck air (CA01648), from the time of filling to the commencement of the classic circulation in November 1996. The five cylinders selected for circulation are indicated by bold type. Numbers in parentheses are the standard deviation of all analyses, except for H<sub>2</sub>, where the number in parentheses is the annual rate of increase of h<sub>2</sub> concentration. the final section of the table presents the analytical precision for the measurement techniques and the target precision for  $\delta^{13}\text{C}$  and CO<sub>2</sub>. for N<sub>2</sub>O, the analytical precision increases from 0.3 ppb at ambient levels to 3 PPB at concentrations greater than 340 PPB due to linearity corrections made in extrapolating the calibration.**

CYLINDER	$\delta^{13}\text{C}$ ‰	$\delta^{18}\text{O}$ ‰	CO <sub>2</sub> ppm	N <sub>2</sub> O ppb	CH <sub>4</sub> ppb	H <sub>2</sub> ppb	CO ppb	H <sub>2</sub> O ppm
CA01648	-7.846(0.009)	-1.264 (0.079)	358.74 (0.19)	311.77 (0.18)	1695.9 (3.1)	531.8 (106.1)	104.7 (0.5)	0.22
CA01609	-6.799 (0.021)	-1.259 (0.117)	320.02 (0.17)	311.82 (0.30)	1696.0 (1.9)	528.3 (19.1)	109.0 (0.6)	0.14
<b>CA01631</b>	<b>-7.752 (0.024)</b>	<b>-2.153 (0.110)</b>	<b>336.49 (0.06)</b>	<b>311.66 (0.10)</b>	<b>1694.4 (1.0)</b>	<b>530.9 (8.8)</b>	<b>107.4 (0.5)</b>	<b>0.30</b>
<b>CA01672</b>	<b>-8.717 (0.022)</b>	<b>-2.751 (0.139)</b>	<b>355.15 (0.08)</b>	<b>312.02 (0.30)</b>	<b>1693.5 (1.0)</b>	<b>533.2 (34.7)</b>	<b>110.6 (0.5)</b>	<b>0.28</b>
<b>CA01608</b>	<b>-9.606 (0.013)</b>	<b>-3.586 (0.063)</b>	<b>378.78 (0.07)</b>	<b>312.05 (0.37)</b>	<b>1689.0 (1.1)</b>	<b>549.0 (70.3)</b>	<b>118.6 (0.5)</b>	<b>0.25</b>
CA01632	-10.480 (0.016)	-4.289 (0.039)	396.18 (0.11)	311.71 (0.13)	1689.2 (0.7)	541.5 (66.2)	133.0 (0.8)	0.25
<b>CA01664</b>	<b>-6.681 (0.021)</b>	<b>-0.963 (0.062)</b>	<b>323.04 (0.08)</b>	<b>403.17 (0.42)</b>	<b>1695.0 (0.8)</b>	<b>528.7 (41.0)</b>	<b>98.9 (0.3)</b>	<b>0.91</b>
CA01691	-7.757 (0.012)	-2.085 (0.068)	339.39 (0.06)	393.82 (0.37)	1694.6 (0.7)	530.0 (5.6)	110.4 (0.1)	0.24
CA01638	-8.709 (0.030)	-2.869 (0.116)	353.33 (0.06)	341.60 (0.38)	1690.8 (0.5)	541.8 (70.5)	114.2 (0.6)	0.23
CA01660	-9.518 (0.037)	-3.581 (0.075)	375.25 (0.33)	404.10 (0.20)	1688.8 (0.5)	539.6 (58.0)	128.8 (1.1)	0.14
<b>CA01685</b>	<b>-10.421 (0.017)</b>	<b>-4.381 (0.105)</b>	<b>394.52 (0.03)</b>	<b>408.77 (0.46)</b>	<b>1689.3 (0.7)</b>	<b>540.9 (12.8)</b>	<b>135.4 (0.7)</b>	<b>0.27</b>
Analytical Precision	0.03	0.06	0.06	0.3 (3)	3.0	3.0	1.0	
TARGET	0.01		0.05					

Five standards were chosen for circulation using the criteria that the full range of CO<sub>2</sub> concentrations is represented and that two of the cylinders with elevated N<sub>2</sub>O concentration were included. These standards are indicated by bold typeface in Table 3.

The isotopic compositions of GS19B and GS20B measured at CSIRO in November 1996 are given in Table 4. CSIRO has separate canisters of both of these gases (designated GS19 and GS20) that have been analysed over many years and were analysed with GS19B and GS20B in November 1996. The isotopic compositions of GS19 and GS20 are also summarised in Table 4. Both sets of these "GS" standards have isotopic compositions near the middle of the range covered by the CLASSIC air standards. Also given in Table 4 are the isotopic compositions assigned to the CO<sub>2</sub> gases in these canisters [13].

**Table 4. Isotopic compositions of the pure CO<sub>2</sub> gases measured in November 1996. (standard deviation in parentheses). The isotopic composition assigned to these two CO<sub>2</sub> gases are given in bold typeface [13].**

Cylinder	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)
GS19	-7.534 (.008)	-0.705 (.026)
GS19B	-7.509 (.019)	-0.655 (.031)
<b>GS19</b>	<b>-7.502 (.025)</b>	<b>-0.193 (.040)</b>
GS20	-8.615 (.011)	-1.429 (.025)
GS20B	-8.610 (.013)	-1.434 (.030)
<b>GS20</b>	<b>-8.622 (.025)</b>	<b>-0.991 (.040)</b>

### 3.1.2 Analysis of the non-circulating standards at CSIRO: 1996–1998

The six non-circulated standards were analysed once during the circulation of the CLASSIC standards, in August 1997, and then in 1998 when the circulating standards returned to CSIRO. All results from the analysis of these standards and the GS19 and GS20 canisters are summarised in Table 5. The differences between measurements before and after the circulation period are given in column 6. For CO<sub>2</sub> there is variation in excess of the analytical precision of 0.06 ppm. For N<sub>2</sub>O the measured differences are within the analytical precision. (At concentrations less than 340 ppb the analytical precision is 0.3 ppb but the extrapolation techniques used to extend the calibration scale to higher concentrations cause the analytical precision to decrease to 3 ppb). Measured  $\delta^{13}\text{C}$  differences between 1996 and 1998 show variation of less than the analytical precision of 0.03 ‰. Measured  $\delta^{18}\text{O}$  differences between 1996 and 1998 are generally within the 0.06 ‰ analytical precision although one cylinder, CA01691, shows a considerably larger difference. Measurements of GS19 and GS20 show slight increases of both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  from 1996 to 1998. For GS19,  $\delta^{13}\text{C}$  increases by 0.024 ‰ and  $\delta^{18}\text{O}$  increases by 0.047 ‰, while for GS20,  $\delta^{13}\text{C}$  increases by 0.025 ‰ and  $\delta^{18}\text{O}$  increases by 0.027 ‰. These increases are less than the analytical precision for these species.

While small changes in the composition of individual standards over the two-year period cannot be excluded, the results suggest that, on average, the standards are stable to the analytical precision.

### 3.1.3 Analysis of the circulating standards at CSIRO: 1996–1998

The results of the CSIRO analysis of the five circulating CLASSIC standards and the GS19B GS20B canisters are presented in Table 6. Analysis at CSIRO in 1996 is identified as CSIRO(1) and analysis at CSIRO in August 1998 is identified as CSIRO(2). The differences between analyses in these two periods are given in column 8 of Table 6. The scatter in the differences for CO<sub>2</sub>, N<sub>2</sub>O,  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  is similar to that observed in the non-circulated standards and for these standards also, we conclude that they are stable for N<sub>2</sub>O, CO<sub>2</sub> and the stable isotopes to within the analytical precision. (Although we again note that small changes in composition of individual standards may have occurred over the two-year period).

**Table 5. CO<sub>2</sub> and N<sub>2</sub>O concentrations, and the CO<sub>2</sub> stable isotopic composition of the non-circulated classic cylinders. The numbers in parentheses are the standard deviation of the measurements made on the cylinder during the analysis period. The values for GS19 and GS20 are from measurements in 1996 when the GS19B and GS20B canisters were analysed.**

		1996 (1995-96 average)	1997	1998	Difference (1998-1996)	Difference (1998-1997)
CO <sub>2</sub> (ppm)	CA01648	358.74 (.19)	358.70 (.06)	358.67 (.04)	-0.07	-0.03
	CA01609	320.02 (.17)	320.06 (.06)	320.13 (.05)	0.11	0.07
	CA01691	339.39 (.06)	339.28 (.11)	339.46 (.09)	0.07	0.18
	CA01638	353.33 (.06)	353.22 (.05)	353.24 (.05)	-0.09	0.02
	CA01660	375.25 (.33)	375.44 (.07)	375.67 (.12)	0.42	0.23
	CA01632	396.18 (.11)	396.27 (.04)	396.33 (.04)	0.15	0.06
N <sub>2</sub> O (ppb)	CA01648	311.77 (.18)	311.57 (.21)	311.84 (.39)	0.07	0.27
	CA01609	311.82 (.30)	311.71 (.28)	311.64 (.49)	-0.18	-0.07
	CA01691	393.82 (.37)	394.02 (.58)	393.70 (.56)	-0.12	-0.32
	CA01638	341.60 (.38)	342.04 (.43)	342.22 (.43)	0.62	0.18
	CA01660	404.10 (.20)	404.67 (.33)	404.32 (.67)	0.22	-0.35
	CA01632	311.71 (.13)	311.87 (.28)	312.06 (.41)	0.35	0.19
$\delta^{13}\text{C}_{\text{VPDB}}$ (‰)	CA01648	-7.846 (.009)	-7.845 (.005)	-7.859 (.006)	-0.013	-0.014
	CA01609	-6.799 (.021)	-6.784 (.026)	-6.782 (.005)	0.017	0.002
	CA01691	-7.757 (.012)	-7.747 (.005)	-7.757 (.011)	0.000	-0.010
	CA01638	-8.709 (.030)	-8.679 (.011)	-8.721 (.013)	-0.012	-0.042
	CA01660	-9.518 (.037)	-9.499 (.013)	-9.513 (.017)	0.005	-0.014
	CA01632	-10.480 (.016)	-10.447 (.011)	-10.460 (.007)	0.020	-0.013
	GS19	-7.534 (.008)	-7.517 (.005)	-7.510 (.012)	0.024	0.007
	GS20	-8.615 (.011)	-8.580 (.012)	-8.590 (.020)	0.025	-0.010
$\delta^{18}\text{O}_{\text{VPDB}}$ (‰)	CA01648	-1.264 (.079)	-1.182 (.033)	-1.259 (.057)	0.005	-0.077
	CA01609	-1.259 (.117)	-1.143 (.095)	-1.236 (.053)	0.023	-0.093
	CA01691	-2.085 (.068)	-2.109 (.084)	-2.236 (.073)	-0.151	-0.127
	CA01638	-2.869 (.116)	-2.721 (.026)	-2.795 (.004)	0.074	-0.074
	CA01660	-3.581 (.075)	-3.440 (.039)	-3.565 (.044)	0.016	-0.125
	CA01632	-4.289 (.039)	-4.329 (.039)	-4.241 (.023)	0.048	0.088
	GS19	-0.705 (.026)	-0.662 (.015)	-0.658 (.014)	0.047	0.004
	GS20	-1.429 (.025)	-1.404 (.022)	-1.402 (.026)	0.027	0.002

**Table 6. Results reported by all laboratories from the analysis of the circulated classic cylinders. The reported N<sub>2</sub>O concentrations from CMDL and SIO have been corrected for scale difference as described in section 2.4. The numbers in parentheses are the standard deviation of the measurements made on the cylinder during the analysis period in each laboratory. Nr indicates no value was reported. The CSIRO(2)-CSIRO(1) difference values are the difference between the analyses at CSIRO.**

	Cylinder	CSIRO(1) 1995-96 Avg	CMDL Apr1997	SIO Dec1997	TU May1998	CSIRO(2) Aug1998	CSIRO(2) - CSIRO(1)
CO <sub>2</sub> (ppm)	CA01664	323.04 (0.08)	323.19 (NR)	323 (NR)	323.10 (.01)	323.11 (.05)	0.07
	CA01631	336.49 (0.06)	336.59 (NR)	337 (NR)	336.55 (.01)	336.57 (.04)	0.08
	CA01672	355.15 (0.08)	355.19 (NR)	355 (NR)	355.23 (.01)	355.19 (.06)	0.04
	CA01608	378.78 (0.07)	378.87 (NR)	379 (NR)	378.84 (.01)	378.77 (.05)	-0.01
	CA01685	394.52 (0.03)	394.64 (NR)	395 (NR)	394.45 (.03)	394.53 (.06)	0.01
N <sub>2</sub> O (ppb)	CA01664	403.17 (0.42)	384.64 (NR)	403.32 (NR)	403.2 (1.2)	403.38 (.55)	0.21
	CA01631	311.66 (0.10)	311.12 (NR)	311.73 (NR)	313.0 (1.4)	311.85 (.22)	0.19
	CA01672	312.02 (0.30)	312.12 (NR)	311.73 (NR)	309.6 (0.3)	311.62 (.30)	-0.40
	CA01608	312.05 (0.37)	311.97 (NR)	311.63 (NR)	310.0 (0.7)	311.66 (.72)	-0.39
	CA01685	408.77 (0.46)	390.38 (NR)	408.56 (NR)	408.2 (0.9)	408.13 (.23)	-0.64
$\delta^{13}\text{C}_{\text{VFDB}}$ (‰)	CA01664	-6.681 (0.021)	-6.645 (.010)	-6.561 (.009)	-6.667 (.028)	-6.657 (.025)	0.024
	CA01631	-7.752 (0.024)	-7.759 (.012)	-7.655 (.016)	-7.803 (.019)	-7.741 (.017)	0.011
	CA01672	-8.717 (0.022)	-8.765 (.010)	-8.649 (.011)	-8.794 (.012)	-8.715 (.014)	0.002
	CA01608	-9.606 (0.013)	-9.641 (.011)	-9.508 (.014)	-9.668 (.023)	-9.597 (.013)	0.009
	CA01685	-10.421 (0.017)	-10.531 (.010)	-10.411 (.007)	-10.578 (.003)	-10.437 (.017)	-0.016
	GS19B	-7.509 (0.011)	-7.517	n/a	n/a	n/a	n/a
	GS20B	-8.610 (0.009)	-8.624	-8.589	-8.637	-8.610 (.016)	0.000
$\delta^{18}\text{O}_{\text{VFDB}}$ (‰)	CA01664	-0.963 (0.062)	-0.824 (.033)	0.068 (.035)	-0.110 (.013)	-0.983 (.045)	-0.020
	CA01631	-2.153 (0.110)	-2.000 (.028)	-1.089 (.029)	-1.323 (.035)	-2.076 (.030)	0.077
	CA01672	-2.751 (0.139)	-2.843 (.017)	-1.934 (.034)	-2.131 (.013)	-2.789 (.017)	-0.038
	CA01608	-3.586 (0.063)	-3.576 (.022)	-2.685 (.025)	-2.859 (.014)	-3.670 (.047)	-0.084
	CA01685	-4.381 (0.105)	-4.376 (.013)	-3.509 (.026)	-3.707 (.029)	-4.348 (.032)	0.033
	GS19B	-0.655 (0.028)	-0.790	n/a	n/a	n/a	n/a
	GS20B	-1.434 (0.023)	-1.580	-0.935	-0.966	-1.445 (.012)	-0.011

Of the two pure CO<sub>2</sub> canisters only GS20B was re-analysed at CSIRO due to the leaking valve on GS19B. The differences in both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of GS20B between 1996 and 1998 are negligible, 0.000 ‰ and -0.011 ‰ respectively, indicating this canister was stable and not compromised during the circulation.

### 3.1.4 Summary of stability

The analyses at CSIRO over the three years indicate that all CLASSIC standards are stable within the analytical precision of the techniques used. For CO<sub>2</sub> and  $\delta^{13}\text{C}$ , differences between the 1996 and 1998 measurements at CSIRO are close to the desired precision targets of 0.05 ppm and 0.01 ‰ respectively. The  $\delta^{18}\text{O}$  results indicate agreement at close to the analytical precision, 0.06 ‰, although the scatter in these measurements is greater than expected.

## 3.2 Reported results from the four laboratories

The results reported by the four laboratories are presented in Table 6. For CO<sub>2</sub> concentrations, the agreement is good, better than 0.1 ppm for all laboratories except SIO. The lack of agreement with SIO arises, most probably, from the reported concentrations being rounded to the nearest integer giving a precision of 1 ppm for these measurements, much poorer than the anticipated precision.

For N<sub>2</sub>O there is good agreement (range of 0.6 ppb) for the ambient level N<sub>2</sub>O standards (CA01631, CA01672 and CA01608) between CSIRO, CMDL and SIO. (The N<sub>2</sub>O concentrations have been adjusted using the scale factors given in Section 2.5). The TU measurements of the ambient concentration standards are up to 2 ppb different from the other laboratory measurements. For the elevated N<sub>2</sub>O standards the agreement is good (range of 0.6 ppb) for all laboratories except CMDL whose reported values are low by about 20 ppb. Subsequent investigation by CMDL has revealed a problem with calibration during the analysis of these standards and that the "correct" concentrations should be about 400 ppb [19]. The reported  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  for the five standards are plotted in Figure 1. There are large differences in the reported  $\delta^{13}\text{C}$  values, far greater than the desired target for  $\delta^{13}\text{C}$  of 0.01 ‰. The range in reported  $\delta^{13}\text{C}$  values increases from 0.12 ‰ for cylinder CA01664 to 0.16 ‰ for cylinder CA01685. The ranges in reported  $\delta^{18}\text{O}$  values are much larger, decreasing from 1.05 ‰ to 0.87 ‰ for the same standards. These differences could originate from a number of sources including the procedures used to convert measurements onto the VPDB-CO<sub>2</sub> scale, different corrections for the presence of N<sub>2</sub>O and differences in the pre-concentration step that includes the cryogenic extraction and normalisation using air standards. The impacts of these are explored below.

## 3.3 Calibration scale offsets

The two canisters of high purity CO<sub>2</sub>, GS19B and GS20B, were included to determine the relative performance of the laboratory calibration procedures without the complications associated with the pre-concentration step, i.e. the extraction of CO<sub>2</sub> from air. Results from the analysis of GS19B and GS20B are given in Table 6. The isotopic composition of GS20B, as reported by all laboratories, is shown in Figure 1 (dashed line) with the measurements of the nearest air standards, CA01672 for  $\delta^{13}\text{C}$  and CA01631 for  $\delta^{18}\text{O}$ . (Even though the measurements of GS19B at CSIRO and CMDL are consistent with the measurements of

GS20B in these laboratories, they are not considered valid as the leaking valve could have influenced these measurements).

The range of the reported  $\delta^{13}\text{C}$  values is much less for GS20B than for the CLASSIC standards, 0.048 ‰ compared with more than 0.12 ‰. For  $\delta^{18}\text{O}$ , the range of reported GS20B values is 0.645 ‰ compared with about 1 ‰ for the CLASSIC standards. The range of the reported GS20B  $\delta^{13}\text{C}$  values is larger than the precision target for merging data and the analytical precision of the measurements. If these differences were observed to be consistent across a range of isotopic compositions, which was the intended use of GS19B, they could be used to correct the reported isotopic compositions of the CLASSIC standards thereby reducing the scatter. The second circulation of the CLASSIC standards will include a second pure  $\text{CO}_2$  sample to assess further the calibration scale offsets indicated by GS20B.

The measurements of GS20B suggest that 40% of the difference in the reported isotopic compositions of the CLASSIC standards arises from the conversion onto the VPDB- $\text{CO}_2$  scale. The remaining difference arises from the specific procedures applied to the CLASSIC standards, i.e. the pre-concentration step, the  $\text{N}_2\text{O}$  correction and, where applicable, the calibration to air standards.

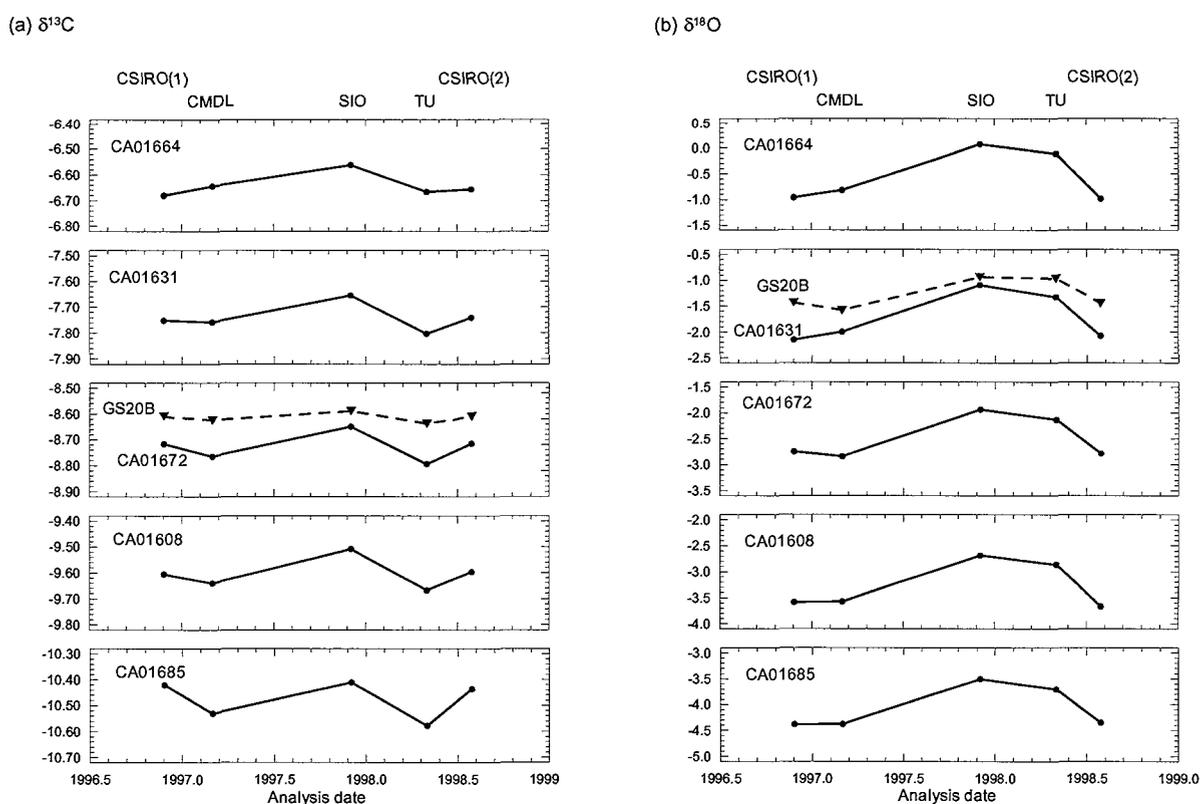


Figure 1. Measured isotopic composition of the  $\text{CO}_2$  in the five circulated CLASSIC standards (solid lines) and GS20B (dashed line). (a)  $\delta^{13}\text{C}$ . (b)  $\delta^{18}\text{O}$ .

### 3.4 N<sub>2</sub>O correction

The N<sub>2</sub>O correction [20] is applied in a similar fashion in each laboratory as:

$$\begin{aligned}\delta^{13}\text{C (corrected)} &= \delta^{13}\text{C} + A \cdot (\text{N}_2\text{O}/\text{CO}_2), \text{ and} \\ \delta^{18}\text{O (corrected)} &= \delta^{18}\text{O} + B \cdot (\text{N}_2\text{O}/\text{CO}_2),\end{aligned}$$

where A is the N<sub>2</sub>O correction factor for contribution to the measured  $\delta^{13}\text{C}$  and B is the N<sub>2</sub>O correction factor for contribution to the measured  $\delta^{18}\text{O}$ . The correction factors, A and B, have been determined experimentally by each laboratory and range from 0.248 to 0.283, and from 0.358 to 0.425, respectively. The magnitude of the applied corrections in the laboratories varies between 0.012 ‰ and 0.044 ‰ for  $\delta^{13}\text{C}$  and between 0.014 ‰ and 0.082 ‰ for  $\delta^{18}\text{O}$ . Differences in A and B reflect the different relative ionisation efficiencies of CO<sub>2</sub> and N<sub>2</sub>O in each mass spectrometer, and the assumed isotopic composition of atmospheric N<sub>2</sub>O. Variation in the relative ionisation efficiency of  $\pm 5\%$  would lead to an error of  $\pm 0.011\%$  and  $\pm 0.015\%$  in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  respectively, much less than the observed differences.

Small differences in the reported N<sub>2</sub>O and CO<sub>2</sub> concentrations, of a few ppb or a few ppm respectively, are not significant. For instance, CMDL reported concentrations almost 20 ppb lower than CSIRO for the two elevated N<sub>2</sub>O standards but if the CMDL concentrations are increased by 20 ppb,  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  would increase by only 0.012 ‰ and 0.021 ‰ respectively. The reported  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  from CMDL for the analyses of these standards were not corrected for this as the changes affected only two standards, were much smaller than the range of differences observed for these standards, and would not change the range of reported compositions for these standards. The N<sub>2</sub>O corrections are not considered to be a significant source of difference at this stage.

### 3.5 The pre-concentration step

The pre-concentration step can be monitored using working air standards, high-pressure cylinders of air with CO<sub>2</sub> isotopic composition that has been assigned following repeated extraction and analysis. The working air standards are analysed for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in exactly the same manner as the CLASSIC standards. The difference between the measured and the assigned isotopic composition of CO<sub>2</sub> extracted from the working air standards is used to correct for variations in the extraction step and the subsequent analysis. We refer to using working air standards in this fashion as "normalisation". Normalisation can also correct for short-term variations in instrument performance. In their calibration strategies, CSIRO, CMDL and TU routinely extract, and analyse, CO<sub>2</sub> from working air standards at the same time as samples are processed while SIO uses CO<sub>2</sub> extracted from air standards during separate CO<sub>2</sub> extraction sessions. To assess the pre-concentration effects further, one of the CLASSIC standards was used to normalise, i.e. correct for pre-concentration effects, the other four CLASSIC standards. This allows the consistent use of working air standards for all laboratories and applies a single N<sub>2</sub>O correction procedure and VPDB-CO<sub>2</sub> scale conversion.

First, cylinder CA01672 was selected as the working air standard because its  $\delta^{13}\text{C}$  isotopic composition was close to that of GS20B. The CSIRO measurements made in 1998 were arbitrarily used to assign the "true" composition of CA01672 as N<sub>2</sub>O = 311.62 ppb, CO<sub>2</sub> = 355.19 ppm,  $\delta^{13}\text{C} = -8.715\%$  and  $\delta^{18}\text{O} = -2.789\%$ . Next, the reported  $\delta 45$  and  $\delta 46$  from each laboratory were used to produce a set of "relative"  $\delta 45$  and  $\delta 46$  differences,  $\Delta 45$  and  $\Delta 46$ , that express the relative isotopic composition difference between each cylinder and CA01672 without any normalisation that may have been applied by the laboratories. Finally, the CSIRO procedures [6, 1] for N<sub>2</sub>O correction, using a relative ionisation efficiency of 0.72,

and conversion onto the VPDB-CO<sub>2</sub> scale were used to convert the  $\Delta 45$  and  $\Delta 46$  into  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . These final values still contain laboratory-specific influences but we make the assumption that these influences are consistent through the measurements reported for each laboratory and are handled equally for all standards by the normalisation.

The relationship to produce the relative delta values was derived from:

$$\delta(2-R) = \delta(1-R) + \Delta(2-1) + \delta(1-R) * \Delta(2-1) / 1000, \quad (1)$$

where  $\delta(1-R)$  is the delta value of gas 1 measured against the reference gas,  $\delta(2-R)$  is the delta value of gas 2 with respect to the reference gas and  $\Delta(2-1)$  is the delta value of gas 2 measured against gas 1. Rearrangement gives the relative difference between cylinders,  $\Delta(2-1)$ , as:

$$\Delta(2-1) = 1000 * (\delta(2-R) - \delta(1-R)) / (1000 + \delta(1-R)). \quad (2)$$

For CSIRO(1), the raw  $\delta 45$  and  $\delta 46$  are from measurements made in November 1996, not from the entire pre-circulation analysis period, to avoid introducing errors from different instrument behaviour over such a long period of time. The raw  $\delta 45$  and  $\delta 46$  values, the calculated  $\Delta 45$  and  $\Delta 46$  values, and the calculated  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values for all standards are given in Table 7 and the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  are plotted in Figure 2. Also plotted in Figure 2 are the reported isotopic compositions (light symbols).

**Table 7. The "raw"  $\delta 45$  and  $\delta 46$  reported by each laboratory, the "relative"  $\delta 45$  and  $\delta 46$  with respect to CA01672 in each laboratory and the "consistent"  $\delta^{13}\text{C}_{\text{VPDB}}$  and  $\delta^{18}\text{O}_{\text{VPDB}}$  after applying the consistent corrections (see text) to the "relative"  $\delta 45$  and  $\delta 46$ .**

	Cylinder	CSIRO(1)	CMDL	SIO	TU	CSIRO(2)
Raw $\delta 45$ (‰)	CA01664	-0.106	30.303	35.489	3.096	-0.131
	CA01631	-1.064	29.253	34.454	2.068	-1.102
	CA01672	-2.009	28.261	33.464	1.135	-2.037
	CA01608	-2.851	27.378	32.609	0.300	-2.876
	CA01685	-3.713	26.449	31.638	-0.648	-3.749
Raw $\delta 46$ (‰)	CA01664	12.161	38.254	28.049	3.889	12.313
	CA01631	11.106	37.157	26.981	2.794	11.334
	CA01672	10.429	36.315	26.132	2.004	10.626
	CA01608	9.782	35.584	25.384	1.293	9.755
	CA01685	8.874	34.680	24.454	0.355	8.969
Relative $\delta 45$ (‰) (wrt CA01672)	CA01664	1.907	1.986	1.959	1.959	1.910
	CA01631	0.947	0.965	0.958	0.932	0.937
	CA01672	0.000	0.000	0.000	0.000	0.000
	CA01608	-0.844	-0.859	-0.827	-0.834	-0.841
	CA01685	-1.707	-1.762	-1.767	-1.781	-1.715
Relative $\delta 46$ (‰) (wrt CA01672)	CA01664	1.714	1.871	1.868	1.881	1.669
	CA01631	0.670	0.812	0.827	0.788	0.701
	CA01672	0.000	0.000	0.000	0.000	0.000
	CA01608	-0.640	-0.705	-0.729	-0.710	-0.862
	CA01685	-1.539	-1.578	-1.635	-1.646	-1.640
Consistent $\delta^{13}\text{C}_{\text{VPDB}}$ (‰)	CA01664	-6.661	-6.582	-6.610	-6.611	-6.656
	CA01631	-7.723	-7.709	-7.717	-7.743	-7.735
	CA01672	-8.715	-8.715	-8.715	-8.715	-8.715
	CA01608	-9.600	-9.614	-9.580	-9.588	-9.589
	CA01685	-10.430	-10.487	-10.490	-10.505	-10.435
Consistent $\delta^{18}\text{O}_{\text{VPDB}}$ (‰)	CA01664	-0.947	-0.790	-0.793	-0.780	-0.992
	CA01631	-2.105	-1.963	-1.948	-1.986	-2.074
	CA01672	-2.789	-2.789	-2.789	-2.789	-2.789
	CA01608	-3.446	-3.511	-3.534	-3.515	-3.667
	CA01685	-4.263	-4.301	-4.359	-4.369	-4.363

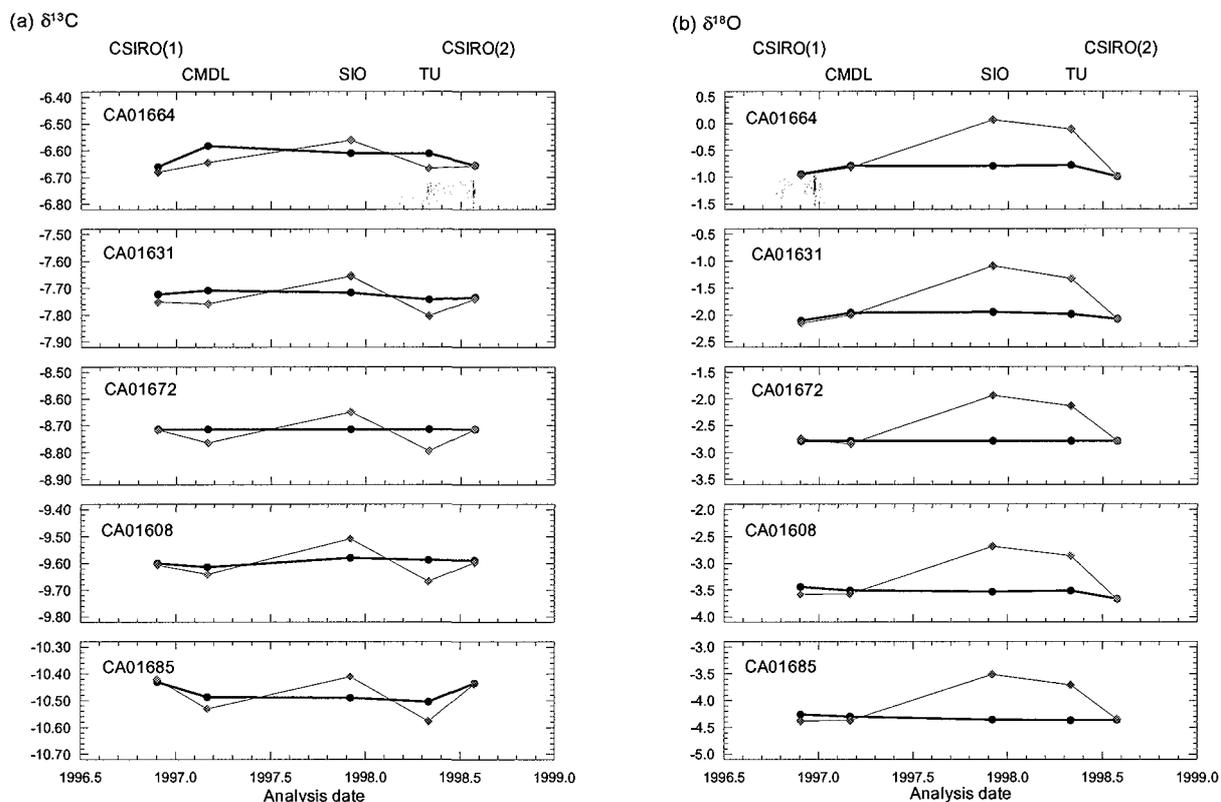


Figure 2. Isotopic composition of the  $\text{CO}_2$  in the five circulated CLASSIC standards after normalisation to cylinder CA01672. (a)  $\delta^{13}\text{C}$ . (b)  $\delta^{18}\text{O}$ . The lighter lines in each panel are the "un"-normalised measurements transferred from Figure 1.

With the large mean offsets between laboratories removed, the ranges of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  for each standard have decreased to 0.055‰, on average, for  $\delta^{13}\text{C}$  and to 0.174‰, on average, for  $\delta^{18}\text{O}$ . The maximum  $\delta^{13}\text{C}$  differences are for cylinders CA01664 and CA01685, the most positive and the most negative standards, with most of the differences being due to the CSIRO measurements. (These two cylinders have the highest  $\text{N}_2\text{O}$  concentrations of the five circulated CLASSIC cylinders but the  $\text{N}_2\text{O}$  contribution to these  $\delta^{13}\text{C}$  differences should be negligible). The average of the CSIRO measurements for cylinder CA01664 is 0.058 ‰ more negative than the average from the other three laboratories and the average of the CSIRO measurements for CA01685 is 0.061 ‰ more positive than the average of the other three laboratories. For  $\delta^{18}\text{O}$ , the maximum difference is observed for cylinders CA01608 and CA01664 with most of the differences arising from the CSIRO measurements.

In Figure 3, the difference between the cylinder  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values calculated for each standard in each laboratory and the average value calculated for each standard is shown. There is a clear indication of significantly different behaviour in the CSIRO measurements, i.e. the CSIRO measurements have a different linearity compared to the other laboratories. We have previously discussed some of the processes that could cause this [21,10] and believe that the CSIRO measurements are affected by mixing of the sample and reference gases in the ion source region of the mass spectrometer. The result of this mixing is an apparent "scale contraction", with measured isotope ratio differences being slightly smaller than they should be. We expect this mixing to occur to some degree in all dual-inlet, isotope ratio mass spectrometers but the CSIRO measurements may be more susceptible because of the small sample size used for analysis. In CSIRO, and possibly in the other laboratories, further

information on past scale contractions may exist in the extensive data archives and a CSIRO study to this end is underway.

#### 4. PRELIMINARY CONCLUSIONS

A suite of ten air standards, high-pressure cylinders of modified marine air, has been prepared and the stability of the air in these standards has been established. The results of the first circulation of five of the standards show interlaboratory differences in  $\delta^{13}\text{C}$  that are much larger than the target precision of 0.01 ‰ and preclude merging global data sets of  $\delta^{13}\text{C}$  at this stage. Using one of the CLASSIC standards to normalise the measurements of the others has reduced the differences but they remain larger than the precision targets.

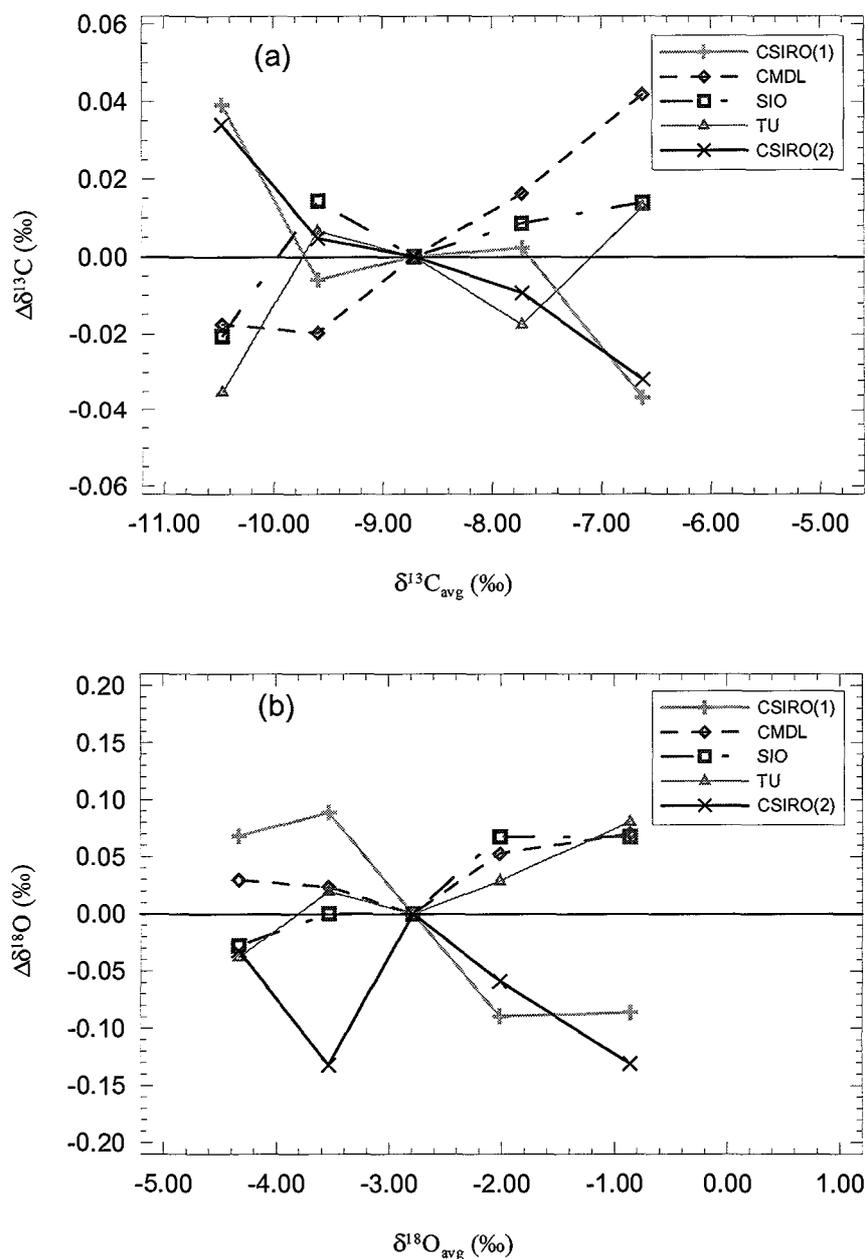


Figure 3. Difference between the normalised isotopic composition for each cylinder, for each laboratory, and the average for that cylinder from all laboratories plotted against the average value for that cylinder: (a)  $\delta^{13}\text{C}$ , (b)  $\delta^{18}\text{O}$ .

Analysis of the canister of pure CO<sub>2</sub>, GS20B, showed that about 40% of the difference in the reported isotopic compositions could be due to the conversion onto the VPDB-CO<sub>2</sub> scale. (In order to determine if this is simply a result of the calculation procedures, the test data suggested by [6] should be processed by each of the participating laboratories. Any inconsistencies that might be identified can then be investigated). The source of the remaining differences is not clear, but there appears to be a measurement scale contraction in at least one laboratory (CSIRO) that is being investigated further.

Some required improvements to intercalibration through the CLASSIC circulation are evident. Firstly, the circulation of the CLASSIC standards should take less than one year. The first circulation took almost two years, more than one year longer than anticipated. The circulation time needs to be reduced to provide information on intercalibration issues at a higher frequency. Secondly, a canister of pure CO<sub>2</sub> has been prepared to replace GS19B to allow more information about each laboratory's calibration scale to be obtained, independently of the pre-concentration procedures. Thirdly, the results from the five standards initially circulated indicate that there is little intercalibration offset arising from the different N<sub>2</sub>O/CO<sub>2</sub> ratios in them. One, or more, of the previously un-circulated standards could be used to test this observation.

The second CLASSIC circulation, commencing in 1999, will provide more information on the stability of the standards, the cylinder-to-cylinder variation measured in each laboratory and the calibration strategies used in the laboratories. Further in the future, it is proposed that the suite of CLASSIC standards play a key supporting role in the GLOBALHUBS strategy [5]. While the CLASSIC high-pressure standards check intercalibration with high precision, they are circulated with low frequency and cannot provide information on the time-scale that a high frequency flask intercomparison program, such as that in operation between CSIRO and NOAA [22], is able to. The GLOBALHUBS strategy includes aspects of CLASSIC and flask intercomparisons and will also allow access by a greater number of laboratories to well characterised air for comparison purposes.

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