# Calibration, comparison and atmospheric records of CO<sub>2</sub> stable isotopic composition Colin Allison<sup>1\*</sup>, Ray Langenfelds<sup>1</sup>, Elise-Andree Guerette<sup>1</sup>, Sylvia Michel<sup>2</sup>, Bruce Vaughn<sup>2</sup>, John Mund<sup>3</sup>, Duane Kitzis<sup>3</sup> Contact: colin.allison@csiro.au

## **Records of the** $\delta^{13}$ **C and** $\delta^{18}$ **O of atmospheric CO**<sub>2</sub> are used

in studies of the global carbon budget. The WMO's Global Atmospheric Watch programme recommends goals (Table 1) for measurement compatibility for participating laboratories (Figure 1).

Component	Network compatibility goal <sup>1</sup>	Extended network compatibility goal <sup>2</sup>	Range in unpolluted troposphere (approx. range for 2019)	Range covered by the WMO scale
CO <sub>2</sub>	0.1 ppm (NH) 0.05 ppm (SH)	0.2 ppm	380 - 450 ppm	250 – 520 <sup>3</sup> ppm
CH <sub>4</sub>	2 ppb	5 ppb	1750 - 2100 ppb	300 - 5900 ppb
CO	2 ppb	5 ppb	30 - 300 ppb	30 - 500 ppb
N <sub>2</sub> O	0.1 ppb	0.3 ppb	325 - 335 ppb	260 – 370 ppb
SF <sub>6</sub>	0.02 ppt	0.05 ppt	9 – 11 ppt	2.0 – 20 ppt
H <sub>2</sub>	2 ppb	5 ppb	400 - 600 ppb	140 –1200 ppb
δ <sup>13</sup> C-CO <sub>2</sub>	0.01‰	0.1‰	-9.5 to -7.5‰ (VPDB)	
δ 18Ο-CO2	0.05‰	0.1‰	-2 to +2‰ (VPDB-CO <sub>2</sub> )	
δ <sup>13</sup> C-CH <sub>4</sub>	0.02‰	0.2‰	-51 to -46‰ (VPDB)	
δ²H-CH4	1‰	5‰	-120 to -63‰ (VSMOW)	
$\Delta^{14}C-CO_2$	0.5‰	3‰	-80 to 20‰	
∆ <sup>14</sup> C-CH <sub>4</sub>	0.5‰		50-350‰	
∆ <sup>14</sup> C-CO	2 molecules cm <sup>-3</sup>		0-25 molecules cm <sup>-3</sup>	
O <sub>2</sub> /N <sub>2</sub>	2 per meg	10 per meg	-900 to -400 per meg (vs. SIO scale)	



Figure 1. Accessed August 2022 from WDCGG. **Table 1.** From GAW Report 255 (https://library.wmo.int/doc num.php?explnum id=10353) (https://gaw.kishou.go.jp/search)

### However, compatibility at the target level has not been demonstrated in independent records of $\delta^{13}$ C (Figure 2a) & $\delta^{18}$ O (Figure 2b) at Kennaook/Cape Grim, Tasmania, or in WMO Round Robin #6 (Figure 3).



**Figure 3**:  $\delta^{13}$ C (left) and  $\delta^{18}$ O (right) results from RR#6. The CSIRO minus INSTAAR difference (inverse of differences in Figure 2) are circled. (Modified from <a href="https://gml.noaa.gov/ccgg/wmorr/index.html">https://gml.noaa.gov/ccgg/wmorr/index.html</a>).

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**Measurement correction and Calibration differences** are the likely sources of the observed differences. The results presented in Figures 2 and 3 were obtained using isotope ratio mass spectrometry (IRMS) and well documented measurement and correction procedures (see Brand et al, (2010, doi:10.1351/PAC-REP-09-01-05) and references therein). However, there are differences in the correction and calibration strategies used in many of these laboratories.

**Correction procedure differences** arise because  $\delta^{13}$ C and  $\delta^{18}$ O values are parameter dependent, i.e. they depend on the measured  $\delta$ 45 and  $\delta$ 46 and parameters used to correct for isobaric interference from <sup>17</sup>O and N<sub>2</sub>O. Key correction equations are given below with the agreed parameters in red, the apparent isotopic composition of N<sub>2</sub>O in green, and parameters that must be measured for each sample or IRMS in **blue**. The final  $\delta^{13}$ C and  $\delta^{18}$ O values are dependent upon many parameters and inconsistencies, or errors, in these parameters can introduce significant bias into comparisons. **Isobaric correction for N<sub>2</sub>O** 

### $\delta 45(\text{corr}) = \delta 45(x_i | VPDB) + \frac{1}{4}$ $-(\delta 45_{\rm C}-\delta 45_{\rm N})$

$$\delta 46(\operatorname{corr}) = \delta 46(x_i | VPDB) + \frac{\rho E}{1 + \rho E} (\delta 46_{\text{C}} - \delta 46_{\text{N}}) \qquad ($$

E is the relative ionisation efficiency of N<sub>2</sub>O wrt CO<sub>2</sub> (~0.7)  $\rho = \frac{1}{CO_2}$ 

### Isobaric correction for <sup>17</sup>O

$r45_{SAMPLE} = (\delta 45(corr) + 1)* r45_{REF}$	$r45 = r^{2}$	
$r46_{SAMPLE} = (\delta 46(corr) + 1)* r46_{REF}$	r46 = 2 r13 = 13	

$$\begin{bmatrix} \frac{r17_{\text{SAMPLE}}}{r17_{\text{REF}}} \end{bmatrix} = \begin{bmatrix} \frac{r18_{\text{SAMPLE}}}{r18_{\text{REF}}} \end{bmatrix}^{\lambda} \qquad \lambda = 0.528$$

$$\delta^{13}C = \begin{bmatrix} \frac{r13_{\text{SAMPLE}}}{r13_{\text{REF}}} - 1 \end{bmatrix} \qquad \delta^{18}O = \begin{bmatrix} \frac{r18_{\text{SAMPLE}}}{r18_{\text{REF}}} - 1 \end{bmatrix} \qquad r$$

**Calibration differences can arise** from the need to establish metrological traceability. Figure 4 (modified from Hibbert, 2006, doi 10.1007/s00769-006-0177-x) illustrates this traceability and suggests increasing uncertainty, and possibly bias, at each step.



Figure 4. Results are comparable if traceable to the same unit.

A Central Calibration Laboratory for CO<sub>2</sub> stable isotopes (CCL-isoCO2) can reduce several steps in the calibration/traceability chain. MPI-BGC acts as the CCL-isoCO2 and provides a calibrated link at the level of secondary standards. The uncertainty of measurements, and the possibility of differing results, is minimised: the pink shading represents the section of the traceability improved by a CCL-isoCO2.



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 $(\delta 45_{\text{C}} - \delta 45_{\text{N}}) \approx 343\%_0$ 

 $(\delta 46_{\rm C} - \delta 46_{\rm N}) \approx 497\%$ 

r13 + 2r17,  $2r18 + 2r13r17 + (r17)^2$ , and  $^{13}C/^{12}C$ , r17 = $^{17}O/^{16}O$ , r18= $^{18}O/^{16}O$ .

 $\cdot 13_{\text{REF}} = r13(\text{VPDB}) = 0.011180$ r17(VPDB) = 0.0003931 $18_{\text{REF}} = r18(\text{VPDB}) = 0.00208835$ 

incertainty for 1	two laboratories: Laboratory 2
	$X_{2}1 \pm s_{1}1$
$s_1^2 + s_1^2 1^2)^{0.5}$ ]	$X_2^2 \pm s_2^2 [ = (s_2^2 + s_2^2)^{0.5} ]$
$s_1^2 + s_1^2 2^{0.5}$ ]	$X_23 \pm s_23 [= (s_2^2 + s_2^2)^{0.5}]$
s <sub>1</sub> <sup>2</sup> + s <sub>1</sub> 3 <sup>2</sup> ) <sup>0.5</sup> ]	$X_24 \pm s_24 $ [ = ( $s_2^2 + s_2^2$ ) <sup>0.5</sup> ]
$(s_1^2 + s_1^2 + s_1^2)^{0.5}]$	$X_25 \pm s_25 [= (s_2^2 + s_2^2)^{0.5}]$

### Has compatibility improved using the CCL-isoCO2 link? The results shown in Figure 2 are updated in Figure 5 with data from both laboratories linked via the CCL-isoCO2 and evaluated using the same agreed (red)

parameters.



For  $\delta^{18}$ O, the two records now meet the goal in Table 1. For  $\delta^{13}$ C, the compatibility goal is still exceeded, with the consistency of the difference suggesting the offset could arise from either (a) the (blue) parameters that must be measured for each sample or IRMS, or (b) a bias introduced by the value assignment at the CCL-isoCO2 level that may be propagated through the different laboratory standards and working reference gases.

### Improved calibration, comparison and compatibility will

require more consistent use of parameters, not just the agreed parameters, and establishing a link through the CCL-isoCO2.

Some suggestions for improving comparisons, and therefore compatibility, are:

- corrections.
- laboratories.
- changed.
- Assessment of traceability and inclusion of a robust uncertainty assessment that can be used to assess laboratory performance against the WMO compatibility goals in a consistent manner.



Figure 5a: Updated  $\delta^{13}$ C records from Kennaook/Cape Grim from CSIRO (green) and INSTAAR (red).

Figure 5b: Updated  $\delta^{18}$ O records from Kennaook/Cape Grim from CSIRO (green) and INSTAAR (red).

• Sharing the agreed, apparent and measured parameters used for the isobaric corrections, including a scheme for the application of the

One, or more, links to the CCL-isoCO2 that can be compared with other

Updating past comparison results when laboratory procedures are

Validation, or revision, of the compatibility goals for stable isotopes of  $CO_2$ .

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