Quantifying combined uncertainties of $\delta^{13}C_{CO2}$ & $\delta^{18}O_{CO2}$ from 20-year calibration datasets: how good could we achieve in realization of VPDB-CO_2 scale via NBS19 etc. carbonates?

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Introduction

Characterizing combined uncertainties of GHGs & related tracers (i.e., $\delta^{13}C_{CO2}$ or $\delta^{18}O_{CO2}$) is required for improving

- Uncertainties in CO_2 flux estimation using atmospheric measurements, and
- Uncertainties in atmospheric trend analysis

WMO community set the targets for the smallest possible bias among datasets/data providers required for these purposes (see Table 1: Recommended network compatibility in *WMO-GAW report #255*).

WMO/GAW Recommended Network Compatibility

Targeted for** *application areas which require the smallest possible bias among different datasets or data providers, such as for the detection of small* ***trends *&* ***gradients***

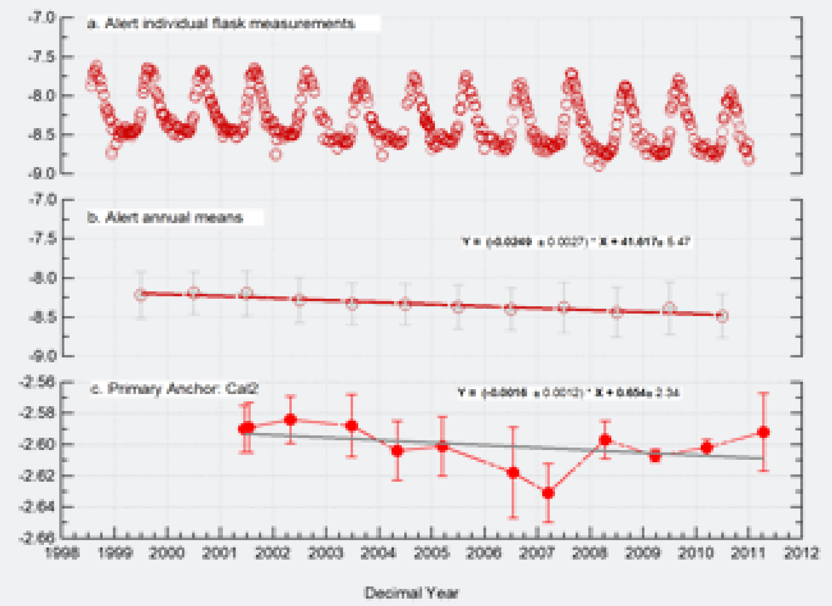
Table 1. Recommended network compatibility of measurements within the scope of WMO/GAW

Component	Network compatibility goal[1]	Extended network compatibility goal[2]	Range in unpolluted troposphere (approx. range for 2019)	Range covered by the WMO scale
CO_2	0.1 ppm (NH) 0.05 ppm (SH)	0.2 ppm	380 - 450 ppm	250 – 520[3] ppm
CH_4	2 ppb	5 ppb	1750 – 2100 ppb	300 – 5900 ppb
CO	2 ppb	5 ppb	30 – 300 ppb	30 - 500 ppb
N_2O	0.1 ppb	0.3 ppb	325 – 335 ppb	260 – 370 ppb
SF_6	0.02 ppt	0.05 ppt	9 – 11 ppt	2.0 – 20 ppt
H_2	2 ppb	5 ppb	400 – 600 ppb	140 –1200 ppb
$\delta^{13}C$-CO_2	0.01‰	0.1‰	-9.5 to -7.5‰ (VPDB)	
$\delta^{18}O$-CO_2	0.05‰	0.1‰	-2 to +2‰ (VPDB-CO_2)	
$\delta^{13}C$-CH_4	0.02‰	0.2‰	-51 to -46‰ (VPDB)	
$\delta^{2}H$-CH_4	1‰	5‰	-120 to -63‰ (VSMOW)	
$\Delta^{14}C$-CO_2	0.5‰	3‰	-80 to 20‰	
$\Delta^{14}C$-CH_4	0.5‰		50-350‰	
$\Delta^{14}C$-CO	2 molecules cm^{-3}		0-25 molecules cm^{-3}	
O_2/N_2	2 per meg	10 per meg	-900 to -400 per meg (vs. SIO scale)	

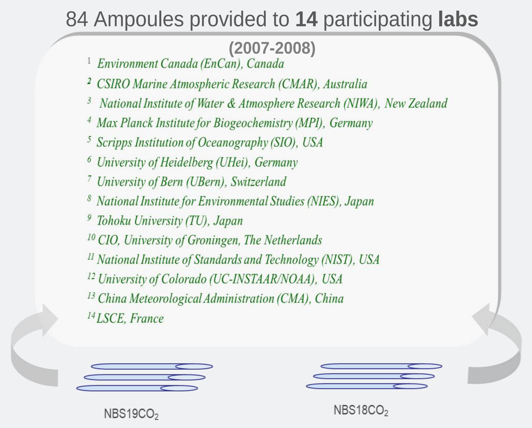
*GAW report #255, 2019

The corresponding values for $\delta^{13}C_{CO2}$ & $\delta^{18}O_{CO2}$ are heighted in green above. Scientists in the community have been working hard to achieve these goals.

An example of requirements for detecting trends in $\delta^{13}C_{CO2}$ at Alert observatory, a global background site. The annual change of the standard is much less than that in atmospheric change at Alert: ***- 0.025 ± 0.003 ‰ /year***



Inter-Comparison *Results of $\delta^{13}C$ & $\delta^{18}O$ in NBS19 & NBS18 CO_2 within WMO Community (2007-2008)



	Avg. $\delta^{13}C$ (2σ)	Avg. $\delta^{18}O$ (2σ)
[1]	**-5.059 ± 0.074‰**	**-23.018 ± 0.394‰**
[2]*	-5.018 ± 0.074‰	-23.018 ± 0.394‰
[3]	-5.070 ± 0.076‰	-23.131 ± 0.486‰
[4]	**-5.056 ± 0.069‰**	**-23.01 ± 0.44 ‰**
[5]*	-5.015 ± 0.069‰	-23.24 ± 0.14 ‰

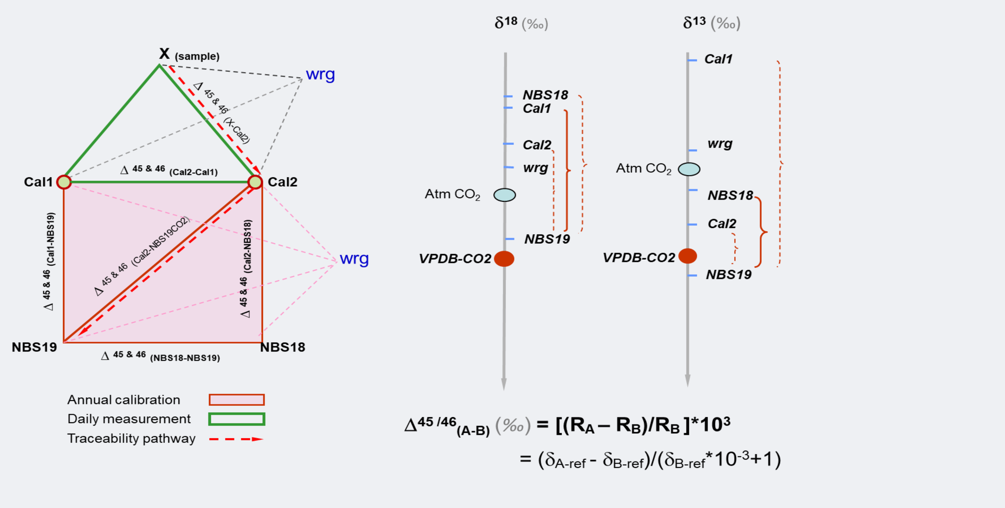
[1] In realization of VPDB-CO_2 scale via NBS19-CO_2 produced by ECCC with **Craig ^{17}O correction (λ = 0.5)**;
[2] the same as [1] with ***Assonov ^{17}O correction (λ = 0.528)**;
[3] In realization of VPDB-CO_2 scale via individual laboratories traceability.
[4] In recommended Table 8 & 10-A of NIST Special Publication 260-149 (2004 Edition) with **Craig ^{17}O correction**
[5] the same as [4] with **λ = 0.528 similar to *Assonov correction in** Table10-D of NIST Special Publications 260-149 (2004)

Assessing the smallest possible bias/difference in $\delta^{13}C_{CO2}$ & $\delta^{18}O_{CO2}$ among multiple labs in WMO /IAEA community when carbonate standard NBS18-CO_2 is measured. The variations well exceed the WMO recommended compatibility targets.

Realization of VPDB-CO_2 scale

the Traceability path in realization of VPDB-CO_2 Scale at ECCC

- An absolute value of **isotope ratio could not be measured precisely** due to changes in physical & chemical processes;
- **A "Relative Deviation"** in isotopic ratio of **two substances can be precisely measured** via an IRMS;
- One-point of "Relative Deviation" is defined (assigned values for NBS19-co2 vs VPDB-co2), **VPDB-CO_2 scale can be realized;**
- Critical to maintain **consistent "relative deviations"** to the primary **NBS19** for robust realization of VPDB-CO_2 scale;
- **Robust realization of VPDB-CO_2 scale** (with specified uncertainties) are important for assessing the WMO recommended network compatibilities for long-term atmospheric measurements.



$\Delta^{45/46}{}_{(A\text{-}B)}$ (‰) = $[(R_A - R_B)/R_B]*10^3$ = $(\delta_{A\text{-ref}} - \delta_{B\text{-ref}})/(\delta_{B\text{-ref}}*10^{-3}+1)$

$\Delta^{45/46}{}_{(X\text{-}VPDB\text{-}CO2)}$ (‰) = $[(R_X/R_{vpdb\text{-}co2}) - 1]*10^3$ = $[(R_X/R_{NBS19\text{-}co2})*(R_{NBS19\text{-}co2}/R_{vpdbCO2}) - 1]*10^3$

Linking atmospheric measurements to the primary scale is through two levels of standards (NBS19-CO_2 & secondary carbonates: NBS18, Cal1 & Cal2) as the traceability path in realization of VPDB-CO_2 scale at ECCC.

Combined Uncertainties of four carbonates on the traceability path

The table at the right shows the **annual means** on "Relative Deviations" of the four carbonates (measured by three IRMSs over 20-years), along the traceability path in realization of VPDB-co2 scale, including $\Delta^{45/46}$ relative to the WRG, $\Delta^{45/46}$ to NBS19-co2 & $\delta^{13}C/\delta^{18}O$ to VPDB-co2, and the **associated uncertainties** at 95% of CL (see the four figures on the right). **Cal2** is the primary anchor for atmospheric measurements.

Combined Uncertainties in Realization of VPDB-CO_2 via **Carbonates** over 20 years through **3 instruments**

Ref.	Δ^{45} (‰)	±2σ (‰)	Δ^{46} (‰)	±2σ (‰)
CO_2 from carbonates vs. *APB2 (WRG) *since 2008				
NBS19	**13.825**	0.026	**7.641**	0.140
NBS18	**6.508**	0.022	**-13.332**	0.163
Cal2	**9.180**	0.047	**-2.911**	0.095
Cal1	**-32.102**	0.070	**-12.590**	0.154

Ref.	Δ^{45} (‰)	±2σ (‰)	Δ^{46} (‰)	±2σ (‰)
CO_2 from carbonates vs. **NBS19-CO_2**				
NBS18	**-7.213**	0.028	**-20.779**	0.316
Cal2	**-4.583**	0.038	**-10.468**	0.176
Cal1	**-45.284**	0.094	**-20.046**	0.302

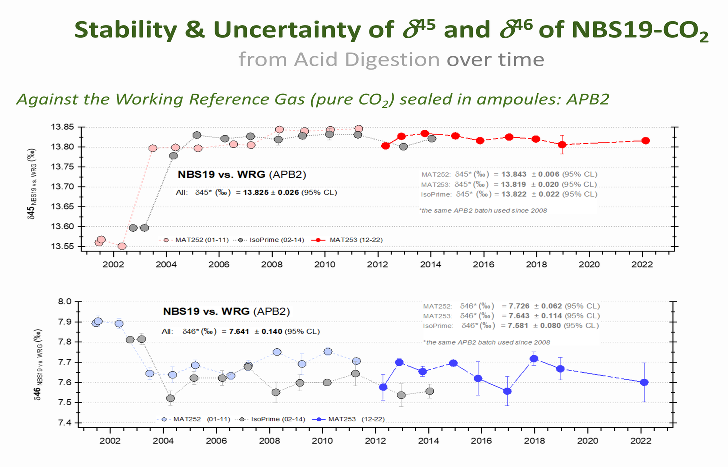
Ref.	$\delta^{13}C$ (‰)	±2σ (‰)	$\delta^{18}O$ (‰)	±2σ (‰)
CO_2 from carbonates vs. VPDB-CO_2				
NBS18	**-5.059**	0.029	**-22.947**	0.323
Cal2	**-2.598**	0.039	**-12.650**	0.166
Cal1	**-45.810**	0.097	**-22.125**	0.300

- Overall, the uncertainties of the realization via carbonates are consistent over time, indicating homogeneity of the standards and the procedures;
- The **combined uncertainties** of the secondary references (carbonates) over 20 years:

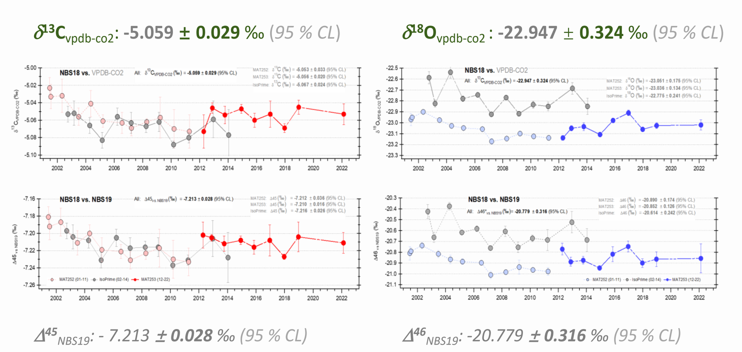
when Δ^{45} ~ 10 ‰, ***U ($\Delta^{45}/\delta^{13}C$): ~ 0.04 ‰*** (95% CL)
when Δ^{46} ~ 10 ‰, ***U($\Delta^{46}/\delta^{18}O$): ~ 0.17 ‰*** (95% CL)

Uncertainties of Relative Deviations in Δ^{45}, Δ^{46} or $\delta^{13}C_{VPDB\text{-}CO2}$, $\delta^{18}O_{VPDB\text{-}CO2}$

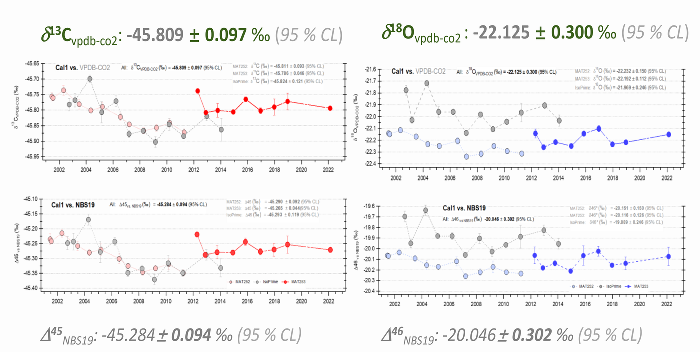
***NBS19* to WRG**



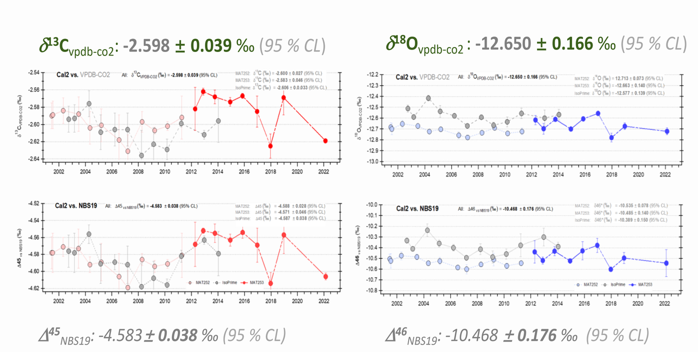
***NBS18* to NBS19**



***Cal1* to NBS19**



***Cal2* to NBS19**



Summary: Take-home message

- Based on the 20-year records in realization of VPDB-CO_2 scale at ECCC using NBS19, NBS18 & other two carbonates (*via three IRMS instruments*), The **combined uncertainties** of the secondary carbonate standards (i.e., *NBS18, Cal2, Cal1) are:*

when Δ^{45} ~ 10 ‰, ***U($\Delta^{45}/\delta^{13}C$): ~ 0.04 ‰*** (95% CL)
when Δ^{46} ~ 10 ‰, ***U($\Delta^{46}/\delta^{18}O$): ~ 0.17 ‰*** (95% CL)

*The **combined uncertainties** of **Cal2** (the primary anchor) via one IRMS instrument (2001-2011):*
U($\Delta^{45}/\delta^{13}C$): ~ 0.03 ‰ (95% CL); ***U($\Delta^{46}/\delta^{18}O$): ~ 0.08 ‰*** (95% CL)

- The **combined uncertainties** over 20-years in the realization of VPDB-CO_2 scale from this work **indicate** the homogeneity of the carbonate standards (including NBS18) and the associated consistent procedures (e.g., acid digestion & IRMS measurements), at the same time implying that meeting the WMO recommended network compatibility targets over time is still challenging.