A Report of $\delta^{13}C$ & $\delta^{18}O$ Measurements in NBS19 & NBS18 pure CO_2: Traceability Uncertainty in CO_2 Isotope Measurements

L. Huang[1], A. Chivulescu[1], C. Allison[2], G. Brailsford[3], W. A. Brand[4], M. Wendeberg[4], A.Bollenbacher[5], R. Keeling[5], I. Levin[6], M. Sabasch[6], M. Leuenberger[7], H. Mukai[8], T. Nakazawa[9], S. Aoki[9], R. Neubert[10], A. Aerts-Bijma[10], M. Verkouteren[11], J. White[12], B. Vaughn[12], S. Michel[12], L. Zhou[13], L.X. Liu[13]

[1] *Environment Canada (EnCan), Canada*

[2] *CSIRO Marine Atmospheric Research (CMAR), Australia*

[3] *National Institute of Water & Atmosphere Research (NIWA), New Zealand*

[4] *Max Planck Institute for Biogeochemistry (MPI), Germany*

[5] *Scripps Institution of Oceanography (SIO), USA*

[6] *University of Heidelberg (UHei), Germany*

[7] *University of Bern (UBern), Switzerland*

[8] *National Institute for Environmental Studies (NIES), Japan*

[9] *Tohoku University (TU), Japan*

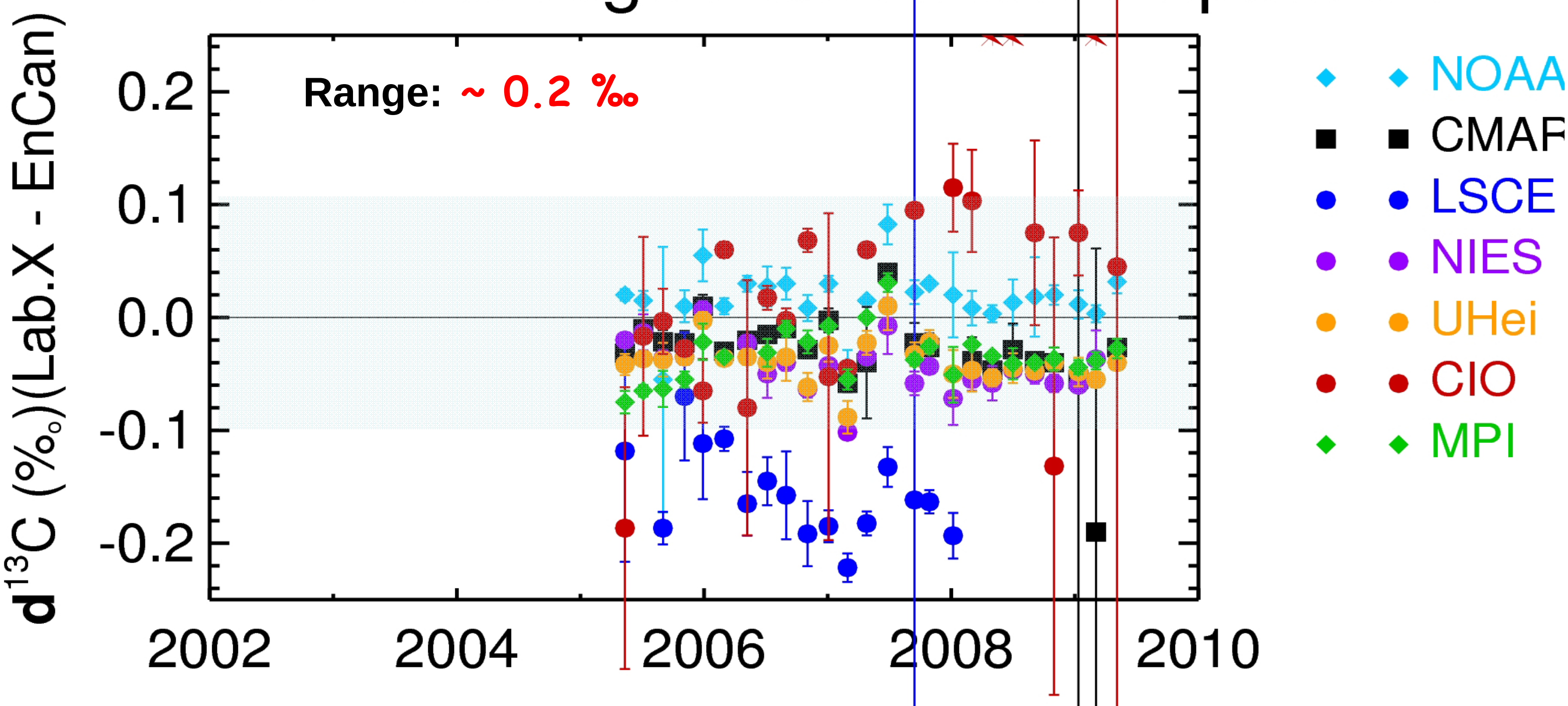
[10] *CIO, University of Groningen, The Netherlands*

[11] *National Institute of Standards and Technology (NIST), USA*

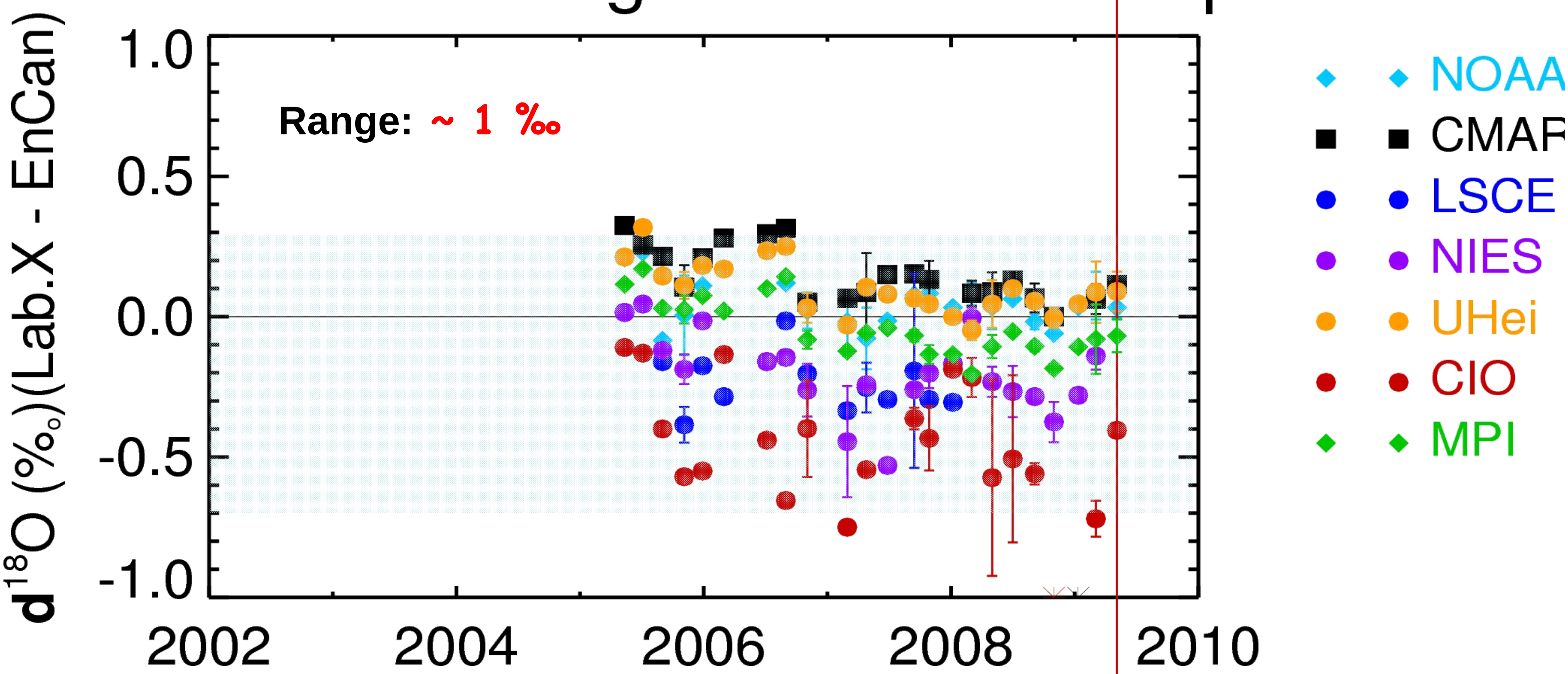
[12] *University of Colorado (UC), USA*

[13] *China Meteorological Administration (CMA), China*

13C Sausage Flask Intercomparison



18O Sausage Flask Intercomparison



One of the main causes for the differences in CO_2 isotope measurements (i.e., $\delta^{13}C$ and $\delta^{18}O$) from inter-comparison exercises, including WMO Round Robin, Cucumber, Sausage and real flasks ICP at Alert, may be

the uncertainty of individual primary anchors on the VPDBCO$_2$ scale

Objectives of this exercise are

- to understand the systematic errors in real air comparisons
- to assess how well the individual primary anchors are close to each other
- to know the limitations of our data comparability

Standard Storage at Our Laboratory

Apparatus used for Acid Digestions of Carbonates

Glass Vacuum System for Acid Digestions of Carbonates & CO_2 Extractions

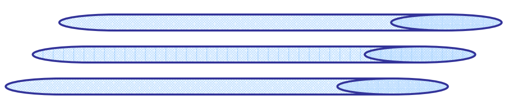
(1)

Glass Vacuum System for Acid Digestions of Carbonates & CO_2 Extractions

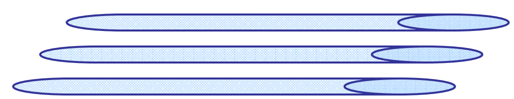
(2)

More than 84 Ampoules sent to 14 participating labs within 10 countries
(During 2007- 2008)

1. *Environment Canada (EnCan), Canada*
2. *CSIRO Marine Atmospheric Research (CMAR), Australia*
3. *National Institute of Water & Atmosphere Research (NIWA), New Zealand*
4. *Max Planck Institute for Biogeochemistry (MPI), Germany*
5. *Scripps Institution of Oceanography (SIO), USA*
6. *University of Heidelberg (UHei), Germany*
7. *University of Bern (UBern), Switzerland*
8. *National Institute for Environmental Studies (NIES), Japan*
9. *Tohoku University (TU), Japan*
10. *CIO, University of Groningen, The Netherlands*
11. *National Institute of Standards and Technology (NIST), USA*
12. *University of Colorado (UC), USA*
13. *China Meteorological Administration (CMA), China*
14. *LSCE, France*



NBS19 CO_2



NBS18 CO_2

Result Report Format & Measurement Protocol

NBS19 & NBS18 pure CO_2 Ampoule Measurements

NBS19 & NBS18 Pure CO2 Ampoules: Produced by **EnCan, Toronto**

Name of Measurement Laboratory: Chemical Science & Technology Laboratory, NIST

Contact name: Michael Verkouteren

Report time: 20/06/2008

Primary anchors on VPDBCO2 scale: the assigned values on VPDBO2 scale for the lab standard gas, i.e. $\delta^{13}C$ = -3.72 per mill vs. VPDB-CO2; $\delta^{18}O$ = -18.49 per mill vs VPDB-CO2

Working Reference Gas: $\delta^{13}C$ = -3.537 per mill vs VPDB-CO2; $\delta^{18}O$ = -15.035 per mill vs. VPDB-CO2

O17 correction used: a= 0.5 K= 0.0091993 (IAEA)

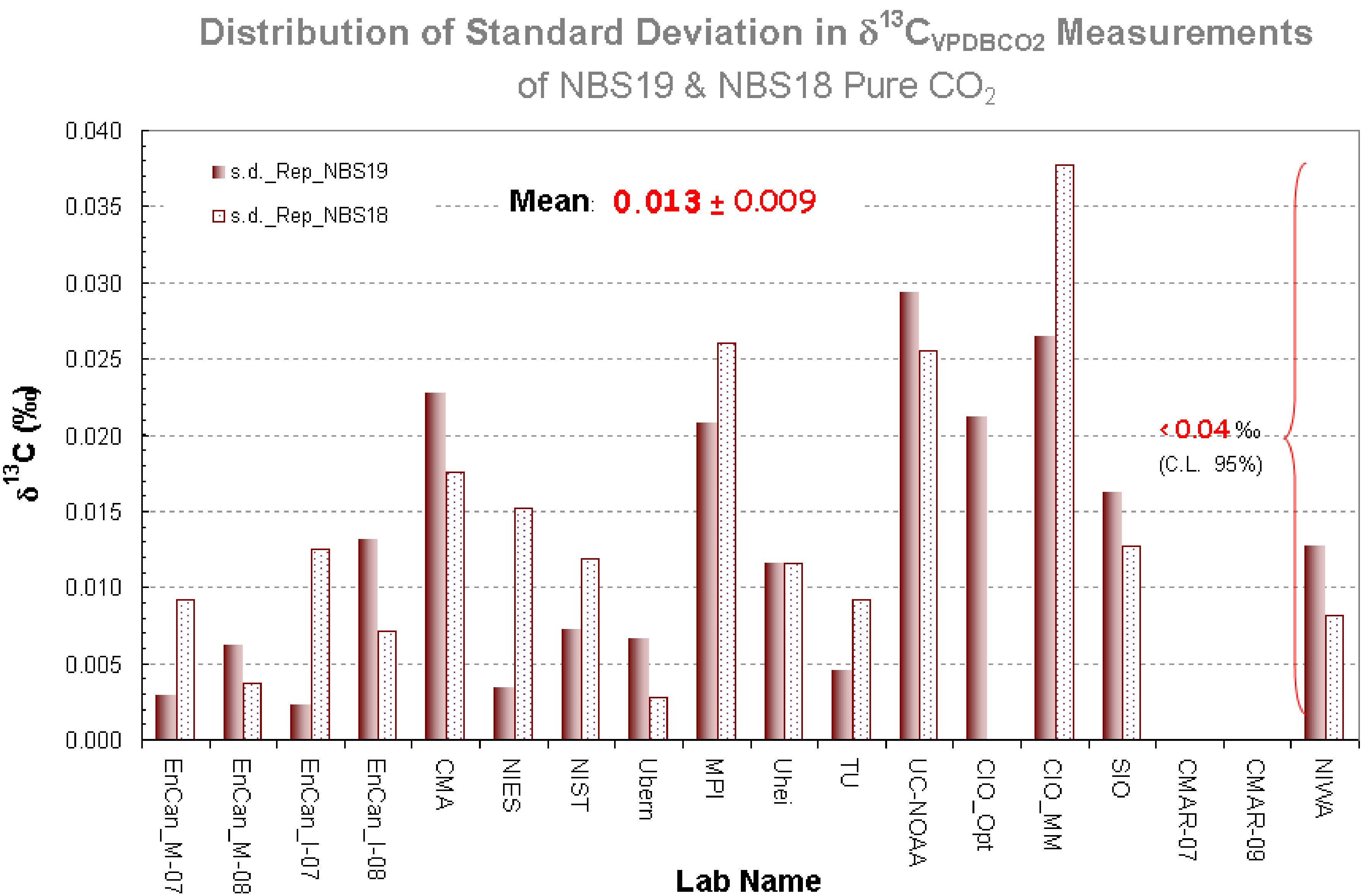
Name	**Analysis Order**	**Date** for IRMS analysis	**Sample ID** indicated on each ampoules' lable	δ^{45} vs.WRG	δ^{46} vs.WRG	$\delta^{13}C$ vs. VPDB-CO2	$\delta^{18}O$ vs. VPDB-CO2	**Comments**
NBS18	1	18/06/2008	#128	-1.592	-8.234	-5.043	-23.162	Each measurement result is an average of three determinations for that sample. Standard uncertainties were <0.01 per mill and <0.02 per mill for d45 and d46, respectively.
NBS19	2	18/06/2008	#158	5.663	12.979	1.961	-2.261	
RM8562	3	18/06/2008	#100339	-0.182	-3.487			
NBS18	4	18/06/2008	#129	-1.621	-8.491	-5.065	-23.415	
NBS19	5	18/06/2008	#160	5.644	12.803	1.947	-2.434	
RM8562	6	18/06/2008	#100391	-0.213	-3.514			
NBS18	7	18/06/2008	#127	-1.595	-8.233	-5.046	-23.161	
NBS19	8	18/06/2008	#159	5.659	12.971	1.957	-2.269	
RM8562	9	18/06/2008	#100511	-0.199	-3.478			
NBS19 (ave)						**1.955**	**-2.321**	
Std						0.007	0.098	
NBS18 (ave)						**-5.045**	**-23.162**	
Std						0.012	0.146	

To allow for normalization, aliquots of RM8564 were also measured (after RM8562) during the sequence. However, the normalization did not significantly alter the measurement results.

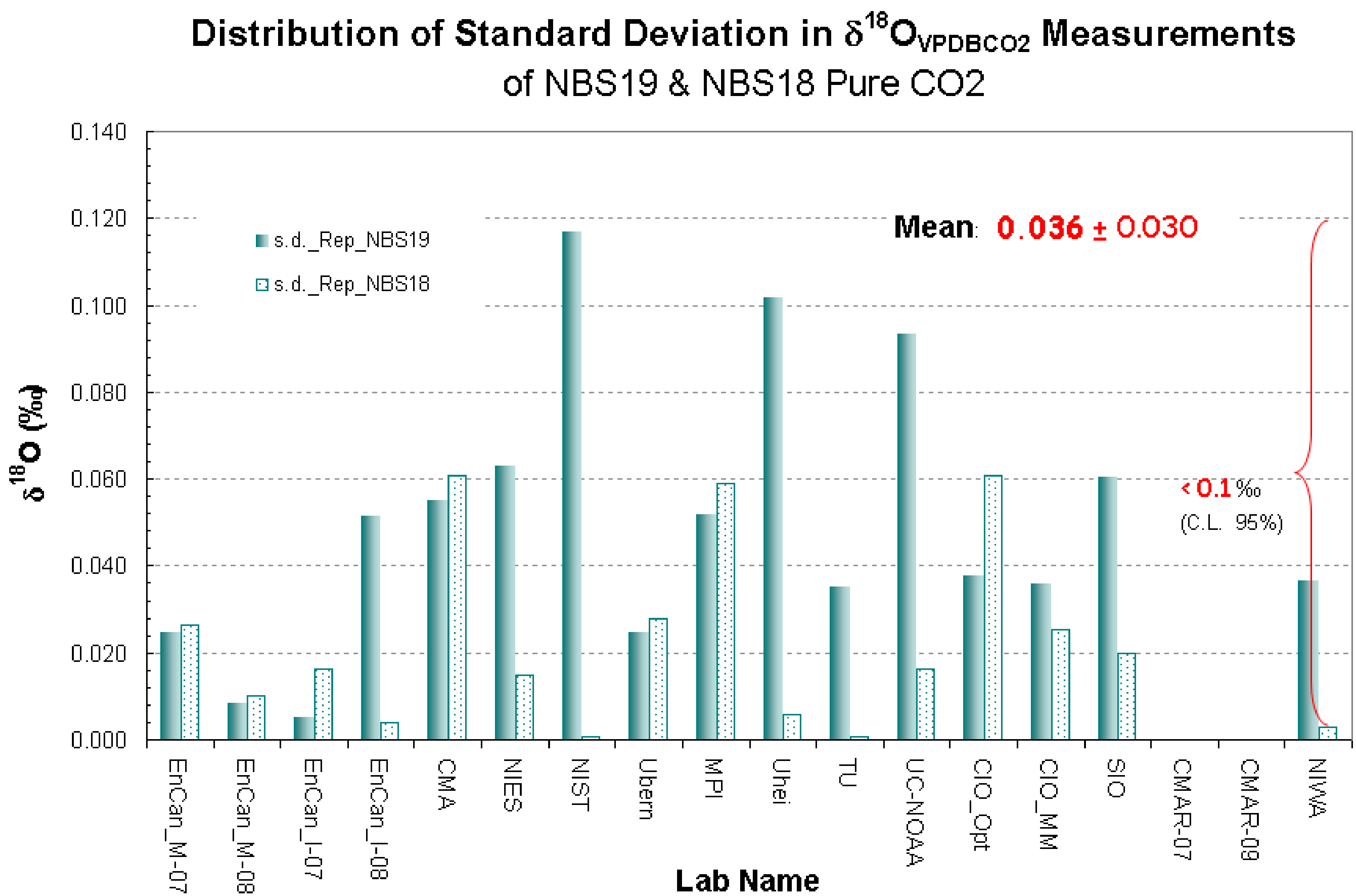
Based on the rule of identical treatment and the procedures suggested in the NIST paper (**p20** for CO_2)

Suggested measurement protocol:

* Lab standard, i..e the primary anchor on VPDB scale, should be measured together with NBS19 & NBS18 ampoules in the order suggested above.
* All the measurements indicated in the table should be performed in a **single day.**
* A single Working Reference Gas (WRG) must be used on the reference side of the inlet.

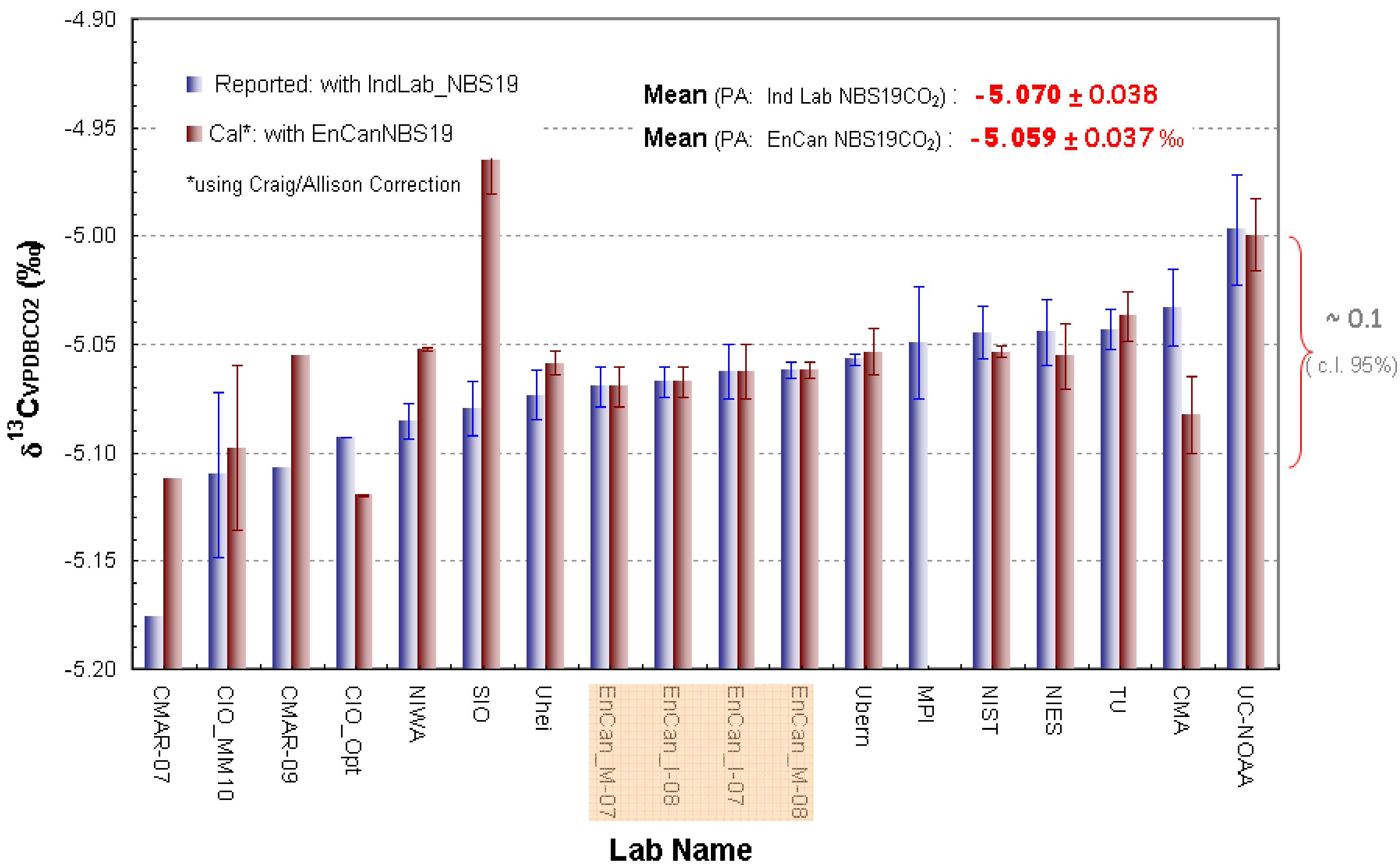


Distribution of Standard Deviation in δ13C VPDBCO2 Measurements
of NBS19 & NBS18 Pure CO2
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
δ13C (‰)
s.d._Rep_NBS19
s.d._Rep_NBS18
Mean: 0.013 ± 0.009
< 0.04 ‰
(C.L. 95%)
EnCan_M-07
EnCan_M-08
EnCan_I-07
EnCan_I-08
CMA
NIES
NIST
Ubern
MPI
Uhei
TU
UC-NOAA
CIO_Opt
CIO_MM
SIO
CMAR-07
CMAR-09
NIWA
Lab Name

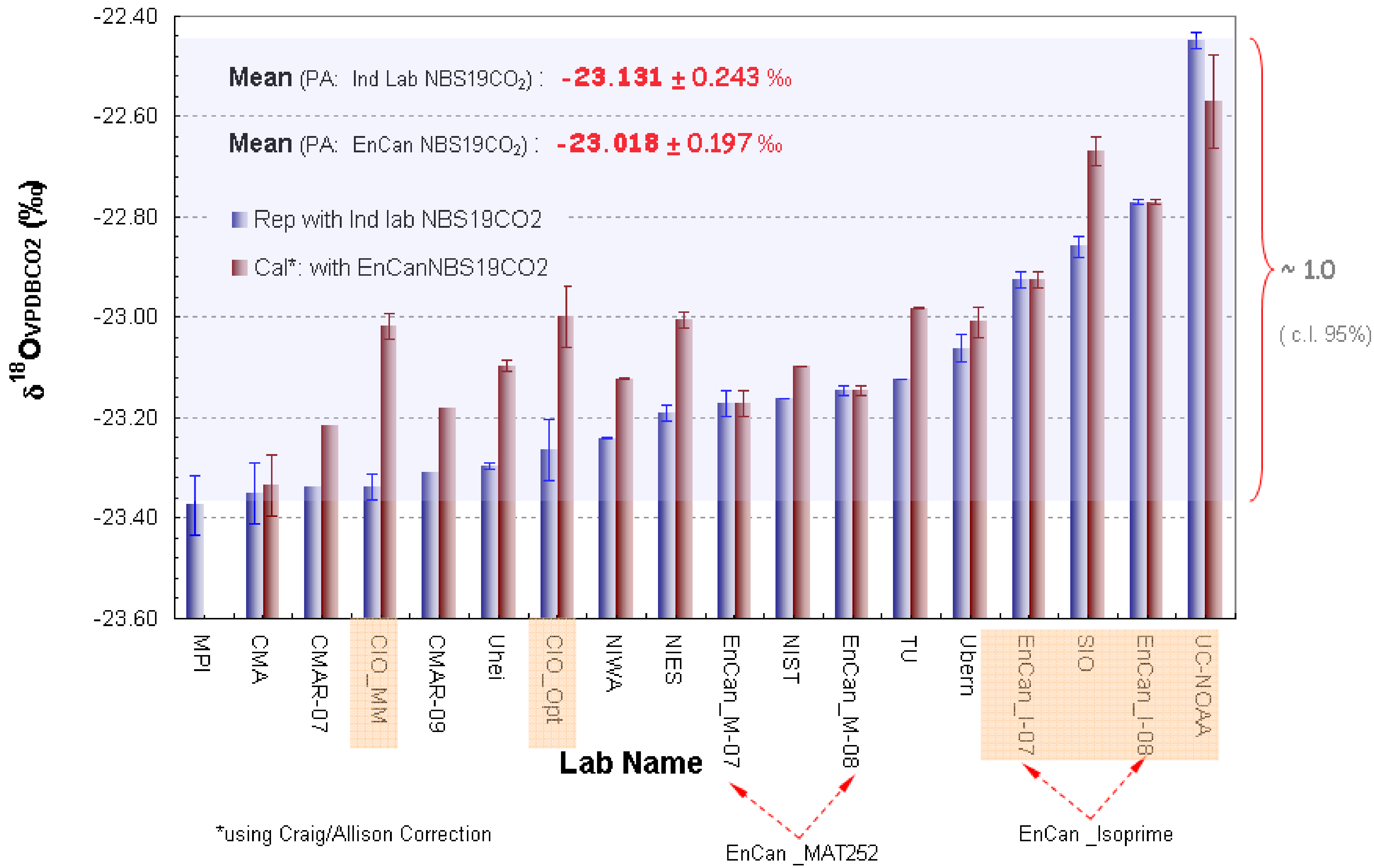


Distribution of Standard Deviation in δ18OVPDBCO2 Measurements
of NBS19 & NBS18 Pure CO2
δ18O (‰)
0.140
0.120
0.100
0.080
0.060
0.040
0.020
0.000
s.d._Rep_NBS19
s.d._Rep_NBS18
Mean: 0.036 ± 0.030
< 0.1‰
(C.L. 95%)
EnCan_M-07
EnCan_M-08
EnCan_I-07
EnCan_I-08
CMA
NIES
NIST
Ubern
MPI
Uhei
TU
UC-NOAA
CIO_Opt
CIO_MM
SIO
CMAR-07
CMAR-09
NIWA
Lab Name

$\delta^{13}C_{VPDBCO2}$ Values of NBS18



$\delta^{18}O_{VPDBCO2}$ Values of NBS18



The Traceability in $\delta^{13}C$ & $\delta^{18}O$ Measurements using EnCan Pure CO_2

$$R_{Lab\text{-}Std}/R_{VPDBCO2} = [R_{LinkStd}/R_{W\text{-}Ref}]*[1/(R_{NBS19CO2}/R_{W\text{-}Ref})]*(R_{NBS19CO2}/R_{VPDBCO2})$$

$$= (\Delta_{LS\text{-}NBS19CO2}*10^{-3}+1)*(R_{NBS19CO2}/R_{VPDBCO2})$$

(where R = Mass 45/44 or 46/44 ratio)

$$[R_{Lab\text{-}Std}/R_{VPDBCO2}]^1 = [\Delta^1_{LS\text{-}NBS19CO2}*10^{-3}+1]*(R^1_{NBS19CO2}/R_{VPDBCO2})$$

→ $[\delta^{45}_{Lab\text{-}Std/VPDBCO2}]^1$, $[\delta^{46}_{Lab\text{-}Std/VPDBCO2}]^1$

$$[R_{Lab\text{-}Std}/R_{VPDBCO2}]^2 = [\Delta^2_{LS\text{-}NBS19CO2}*10^{-3}+1]*(R^2_{NBS19CO2}/R_{VPDBCO2})$$

→ $[\delta^{45}_{Lab\text{-}Std/VPDBCO2}]^2$, $[\delta^{46}_{Lab\text{-}Std/VPDBCO2}]^2$

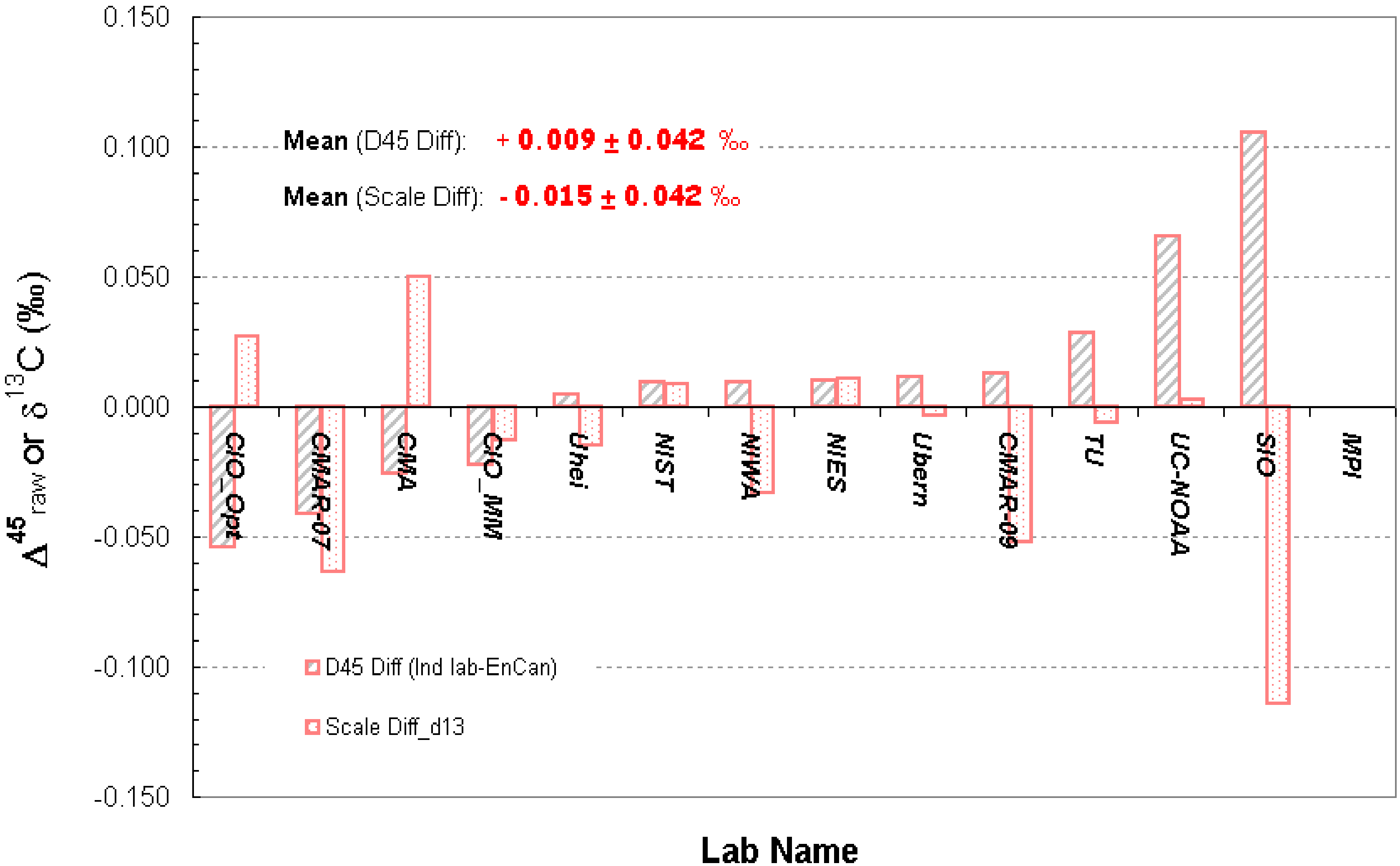
Systematic Error includes

$$[(\Delta^1_{LS\text{-}NBS19CO2}*10^{-3}+1) - (\Delta^2_{LS\text{-}NBS19CO2}*10^{-3}+1])]$$ → IRMS difference

\+

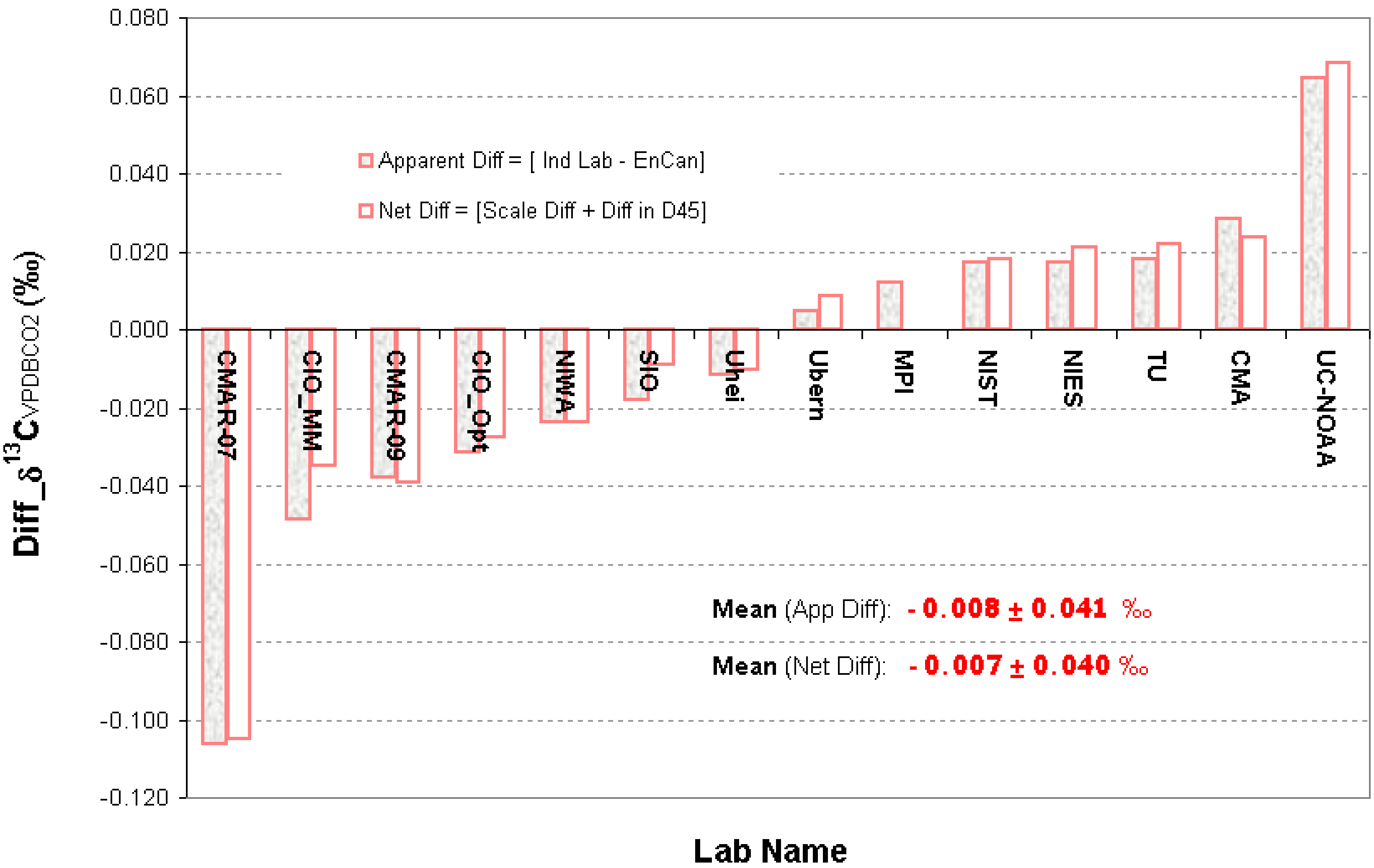
$$[(R^1_{NBS19CO2}/R_{VPDBCO2}) - (R^2_{NBS19CO2}/R_{VPDBCO2})]$$ → Scale difference

Contributions to Systematic Error in $\delta^{13}C$ Measurements of NBS18 Pure CO_2 (Individual lab - EnCan)

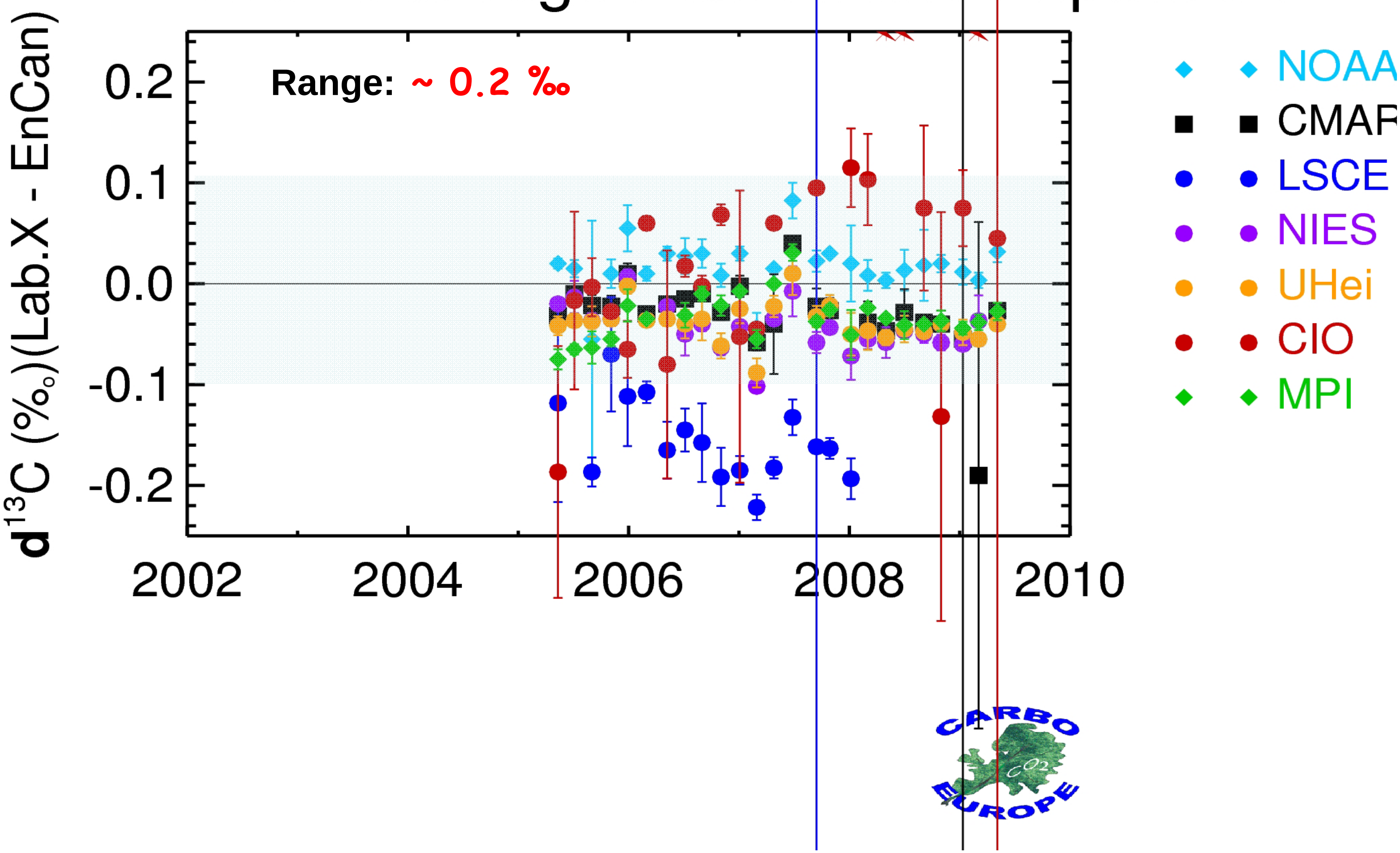


Systematic Errors in $\delta^{13}C$ Measurements of NBS18 Pure CO_2

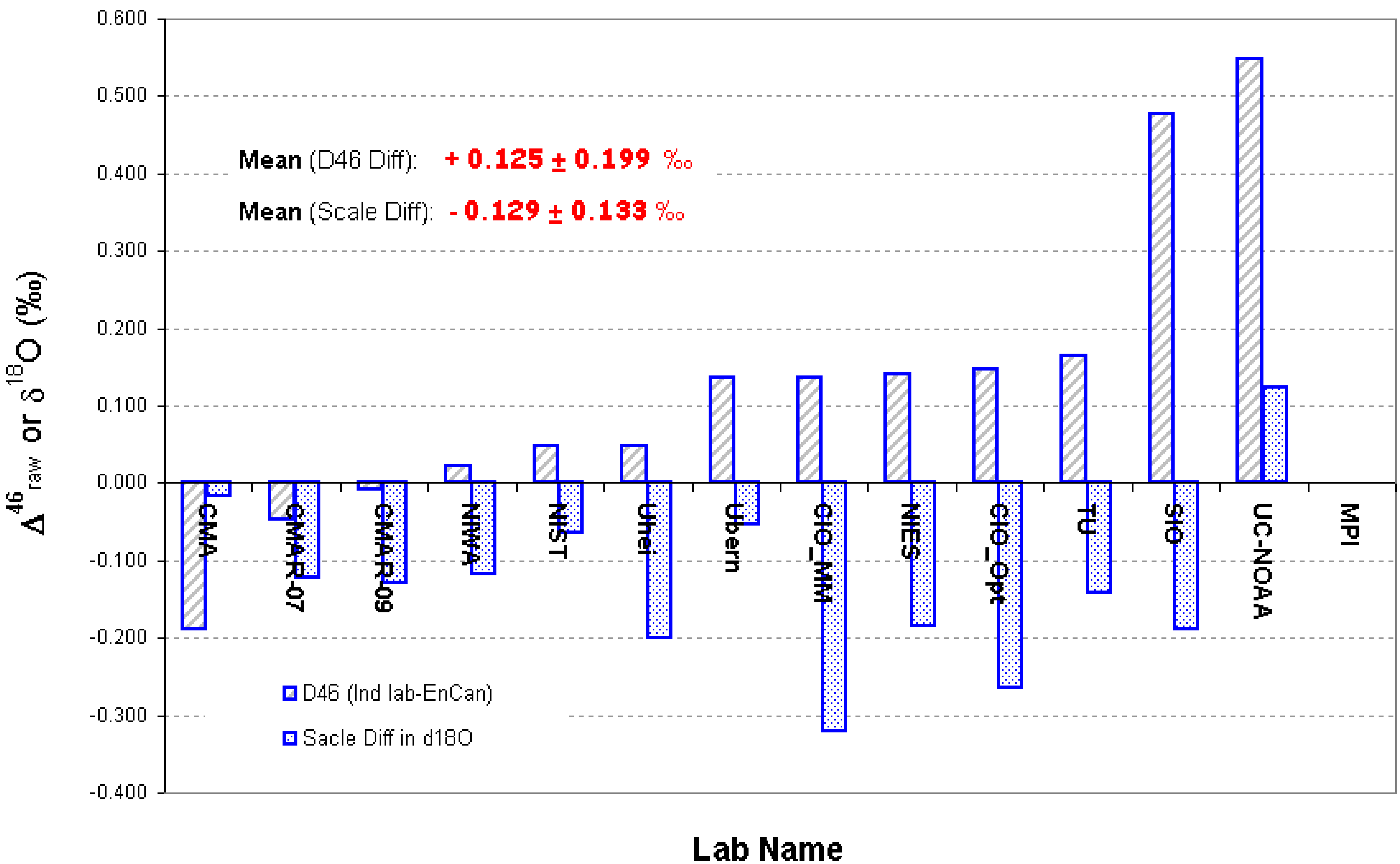
(Individual lab - EnCan)



13C Sausage Flask Intercomparison

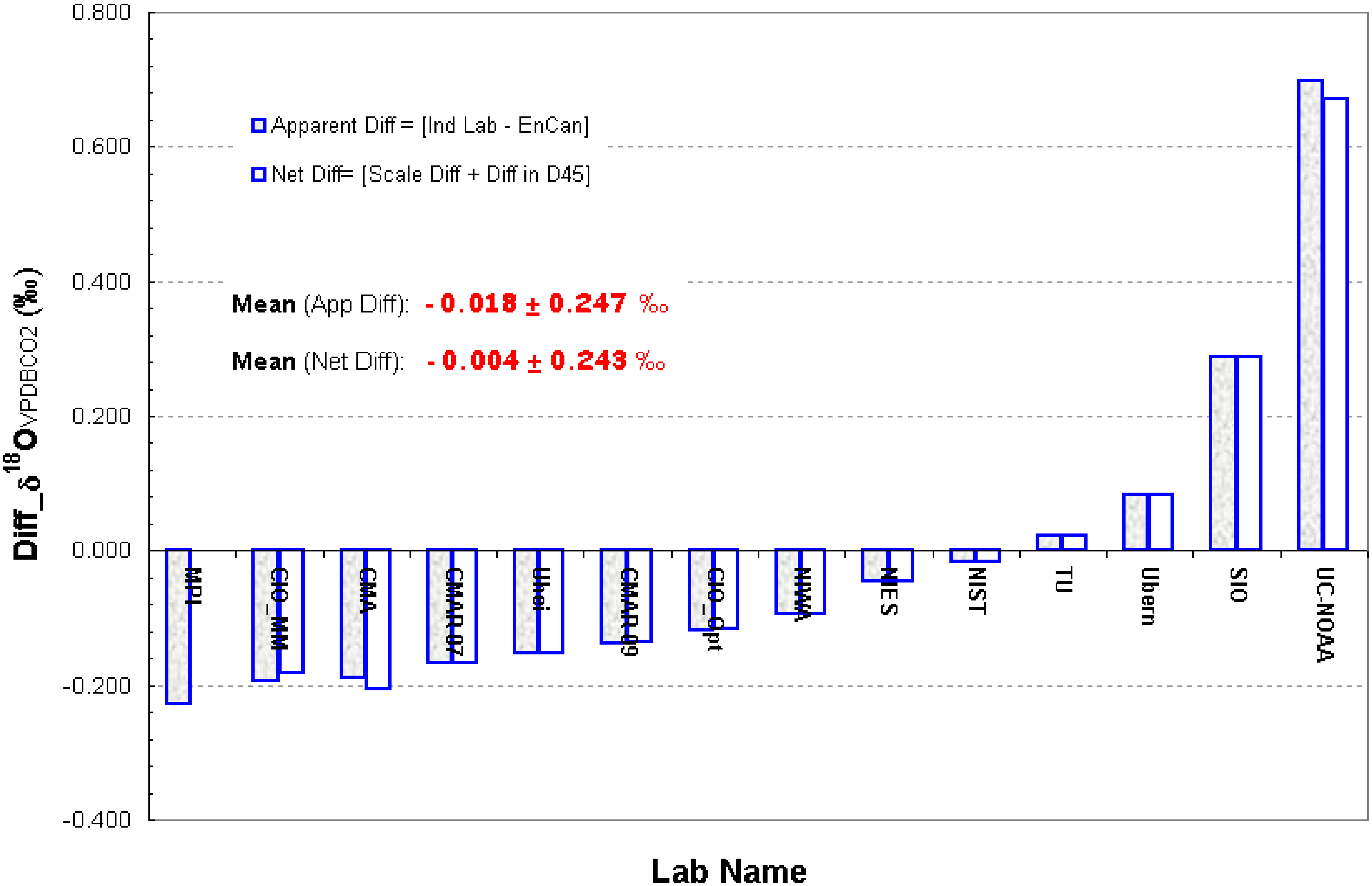


Contributions to Systematic Error in $\delta^{18}O$ Measurements of NBS18 Pure CO_2 (Individual lab - EnCan)

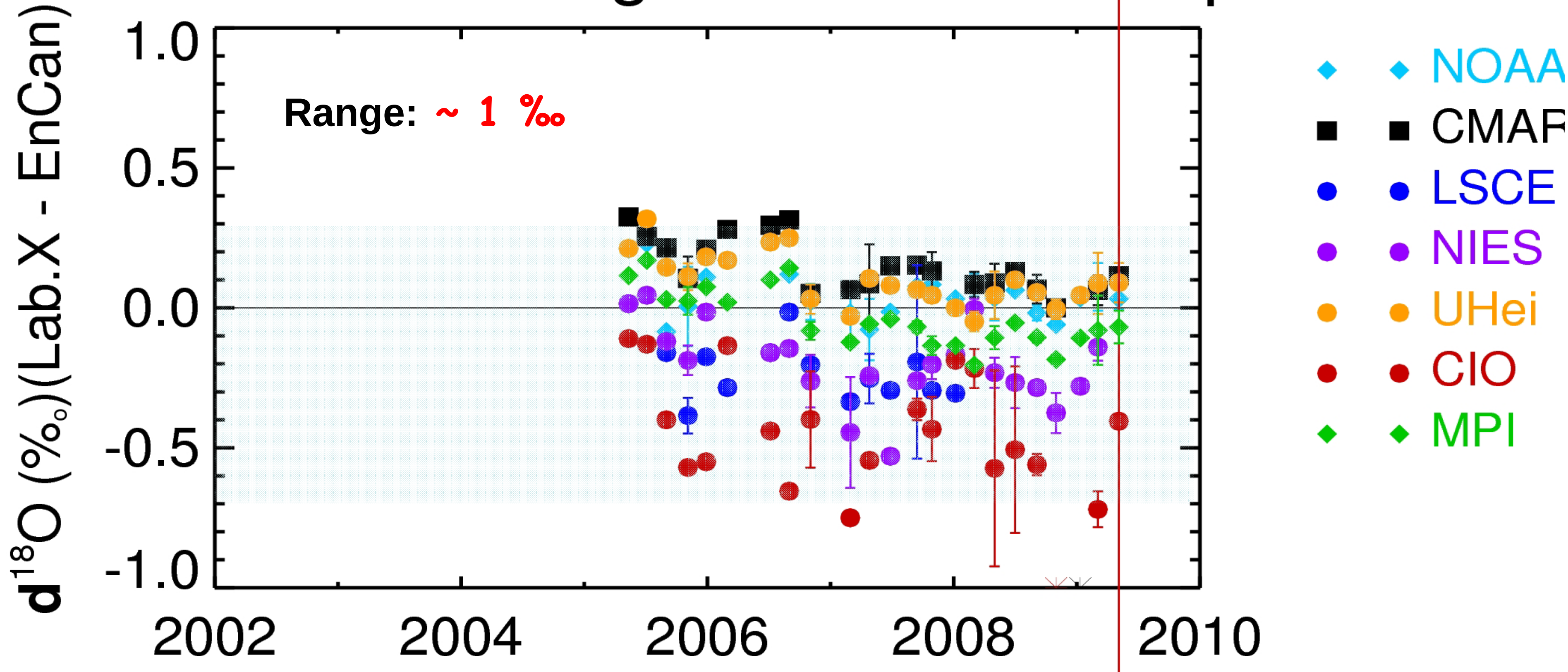


Systematic Errors in $\delta^{18}O$ Measurements of NBS18 Pure CO_2

(Individual lab - EnCan)



18O Sausage Flask Intercomparison



Summary

- The mean values of s.d. (for $\delta^{13}C$ and $\delta^{18}O$) in individual NBS19CO_2 and NBS18CO_2 packages from the 13 labs are < **0.02‰** in $\delta^{13}C$ and < **0.05** ‰ in $\delta^{18}O$, implying that the mean uncertainties caused by the duplicated carbonate productions and corresponding IRMS analysis are relatively small.

- Using the NBS19CO_2 prepared by EnCan as the primary anchor (with Craig/Allison O^{17} correction), the mean values of NBS18CO_2 in $\delta^{13}C$ and $\delta^{18}O$ from the 13 labs are **-5.059**±0.**037**‰ and **-23.018**±**0.197**‰, respectively, on the VPDBCO_2 scale, which are very close to the corresponding results (**-5.06** ± **0.03**‰ and **-23.01** ± **0.22**‰) reported by NIST in the Special Publication 260-149.

- Using NBS19CO_2 prepared at individual labs as the primary anchors, the mean values of NBS18CO_2 in $\delta^{13}C$ and $\delta^{18}O$ from the 13 labs are **-5.070** ± **0.038**‰ and **-23.131** ± **0.243**‰, respectively, indicating that the ranges of scattering in these primary anchors are much larger than the targets (±0.01 ‰ in $\delta^{13}C$ and ±0.05‰ in $\delta^{18}O$) set by WMO Expert meetings for data comparability.

- The differences in $\delta^{13}C$ and $\delta^{18}O$ between two individual labs (apparent differences) are mainly contributed by two factors: one is the difference in the primary scale (due to the variations of primary anchors); another is the difference caused by IRMS, which cause scale contraction or expansion. Usually the sum of the two factors is approximately equal to the apparent difference. This issue may be addressed by the two points anchored on the primary scale.

Question?

Why are the differences in real flask comparisons generally smaller than the corresponding differences shown in this exercise?

Impacts of O^{17} Correction on $\delta^{13}C$ and $\delta^{18}O$ values of $NBS18CO_2$

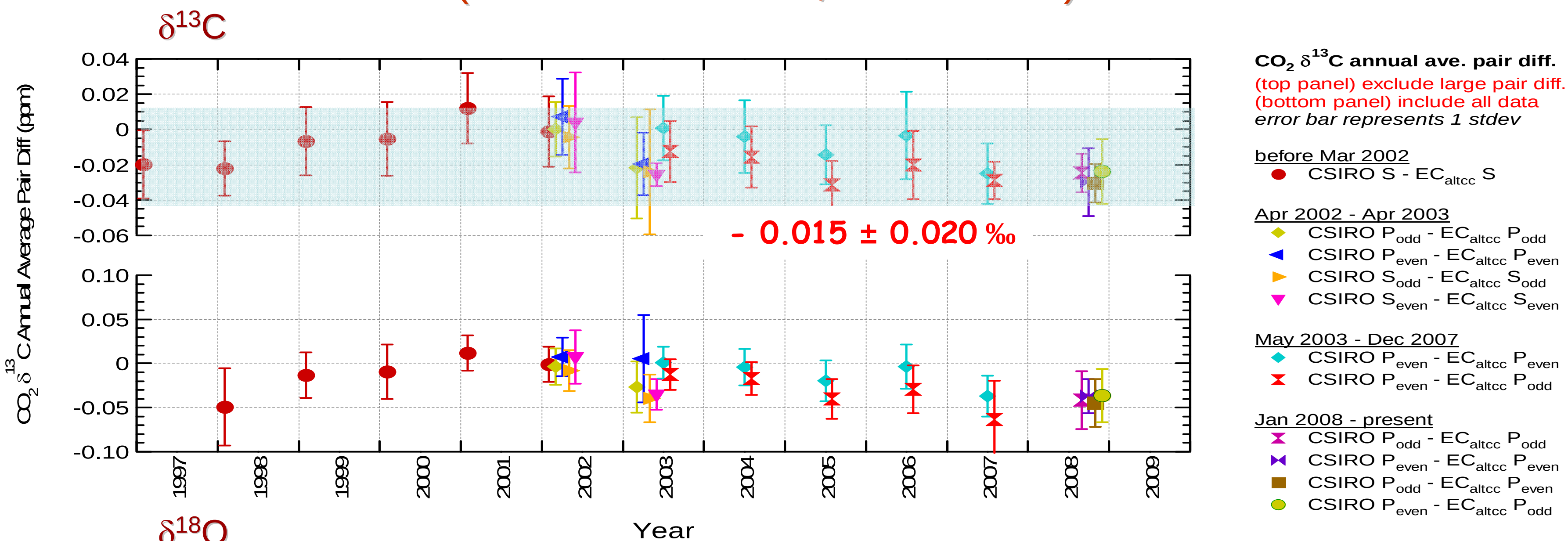
NIST in the Special Publication 260-149, 2004 Edtion

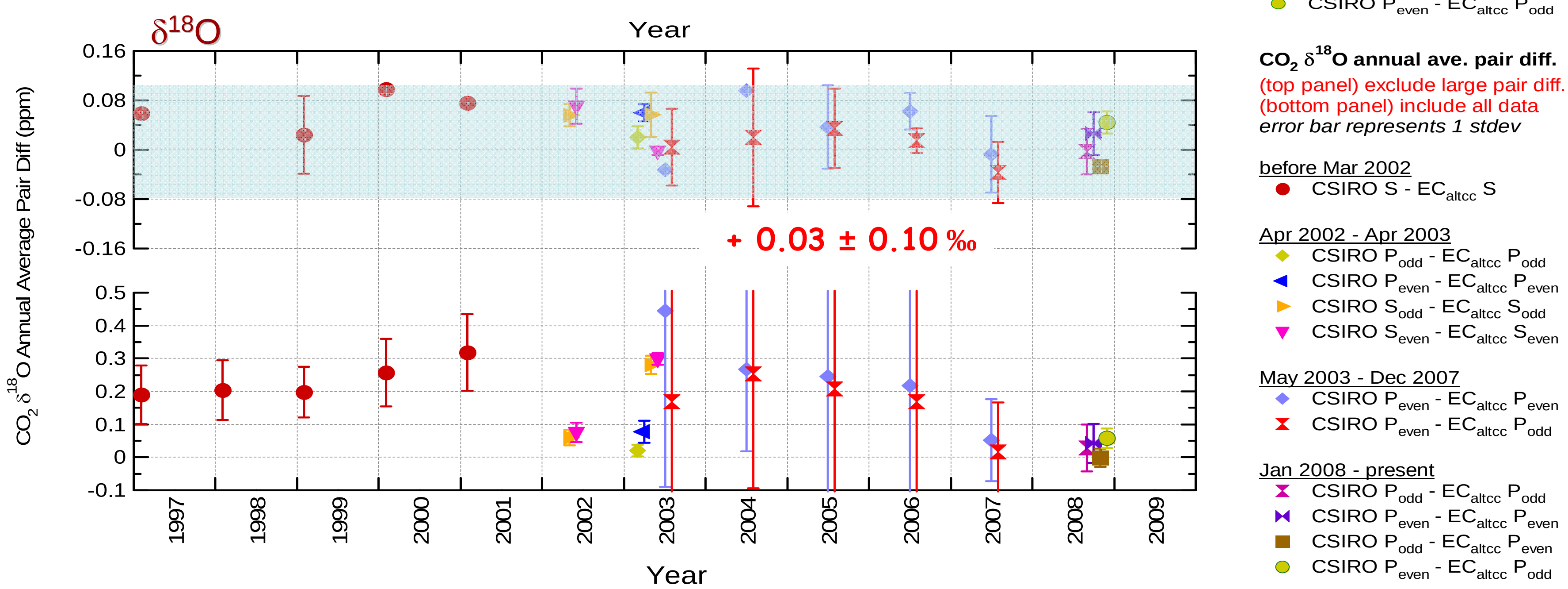
O17 Correction	δ^{13}**C**_ mean	c.s.u*	δ^{18}**O**_ mean	c. s.u*
	vs. VPDB-CO2		vs. VPDB-CO2	
Set A: Craig/Allison *lambda=0.5* *S17=0.000378866601* *S18=0.002067160680* *K=0.0083329582*	**-5.06**	0.03	**-23.01**	0.22
Set B: *lambda= 0.516* *S17= 0.0003799* *S18= 0.0020052* *K= 0.0093703524*	**-5.03**		**-23.24**	
Set C: Santrock *lambda= 0.516* *S17= 0.000402326* *S18= 0.0020052* *K= 0.0099234991*	**-5.02**		**-23.24**	
Set D: Assonov *lambda= 0.528* *S17= 0.000386913* *S18= 0.0020052* *K= 0.0102819162*	**-5.01**		**-23.24**	

*** c.s.u:** Combined standard uncertainty

Annual Means of ICP Pair Differences in $\delta^{13}C$ & $\delta^{18}O$ at Alert

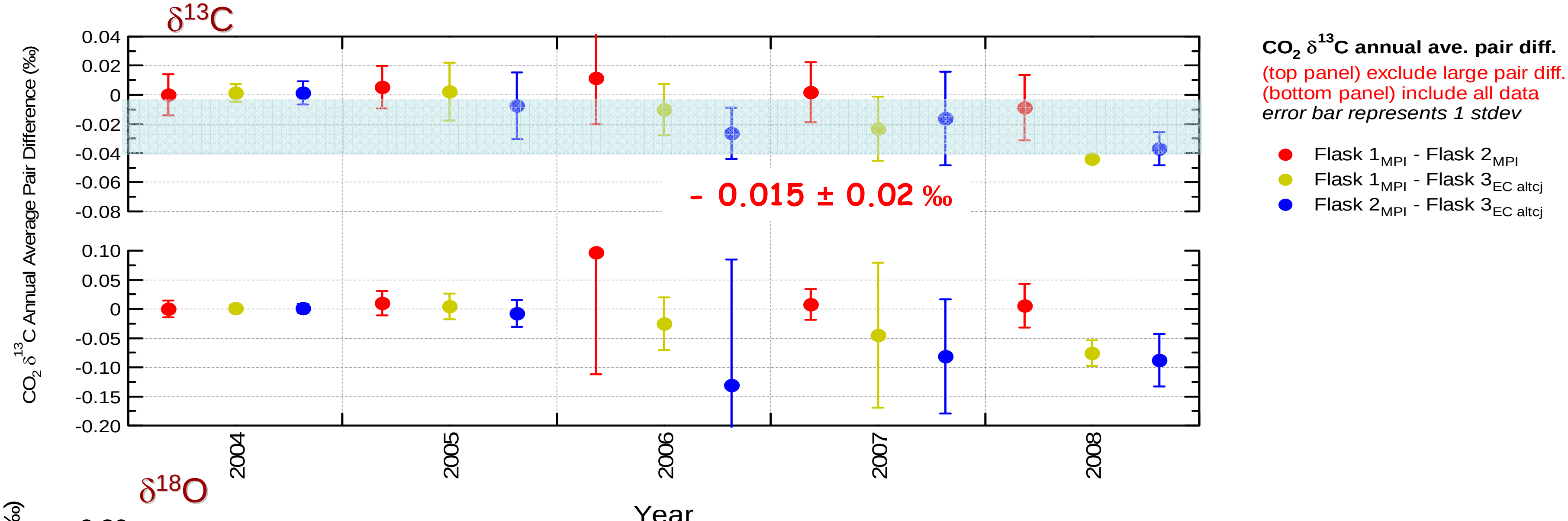
(CMAR and EnCan, 1997 - 2009)

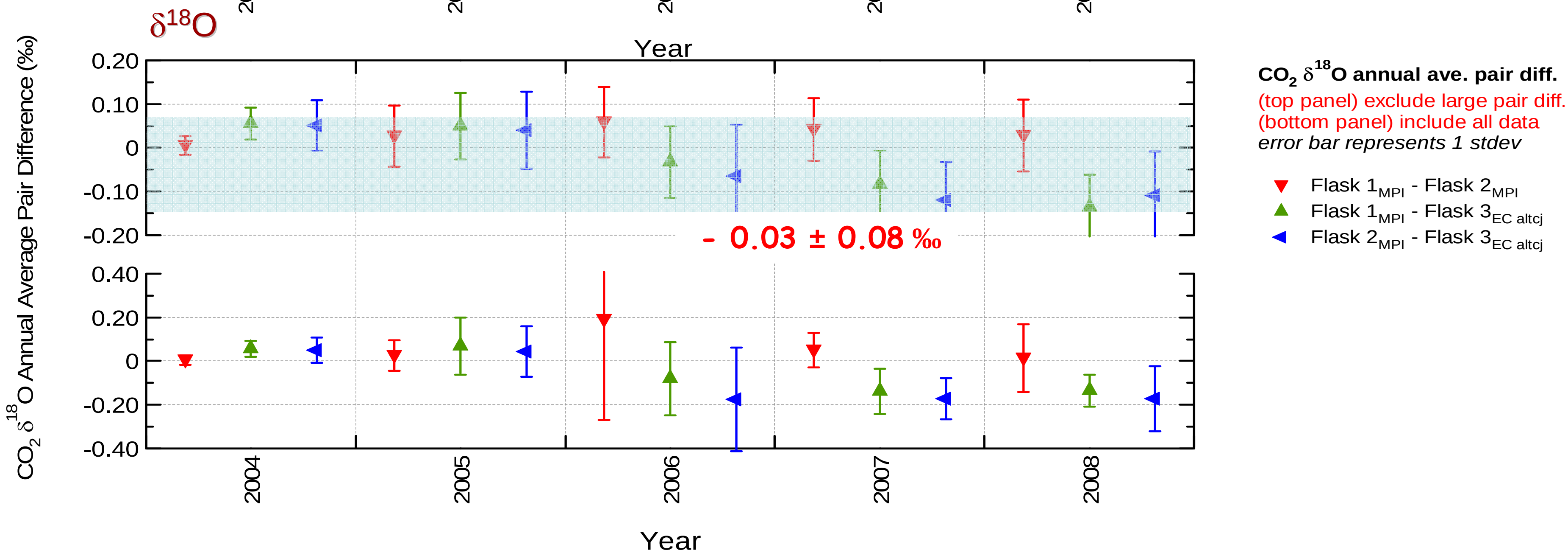




Annual Mean of ICP Pair Differences in $\delta^{13}C$ & $\delta^{18}O$ at Alert

(MPI and EnCan, 2004 - 2009)





Annual Mean of ICP Pair Differences in $\delta^{13}C$ & $\delta^{18}O$ at Alert

(NOAA, UHei and EnCan, 1998 - 2009)