

# Traceability Maintenance via Multi-Carbonates in High Precision Isotope Measurements ( $\delta^{13}\text{C}_{\text{VPDB-CO}_2}$ & $\delta^{18}\text{O}_{\text{VPDB-CO}_2}$ )

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# Traceability in Stable Isotope Measurements in our lab

## Annual Calibration:

$$\begin{aligned} R_{\text{Link-Std}}/R_{\text{VPDBC}^{18}\text{O}_2} &= [R_{\text{LinkStd}}/R_{\text{W-Ref}}] * [1/(R_{\text{NBS19CO}_2}/R_{\text{W-Ref}})] * (R_{\text{NBS19CO}_2}/R_{\text{VPDBC}^{18}\text{O}_2}) \\ &= [\Delta_{\text{LS-NBS19CO}_2} * 10^{-3} + 1] * (R_{\text{NBS19CO}_2}/R_{\text{VPDBC}^{18}\text{O}_2}) \end{aligned}$$

## Daily Measurement:

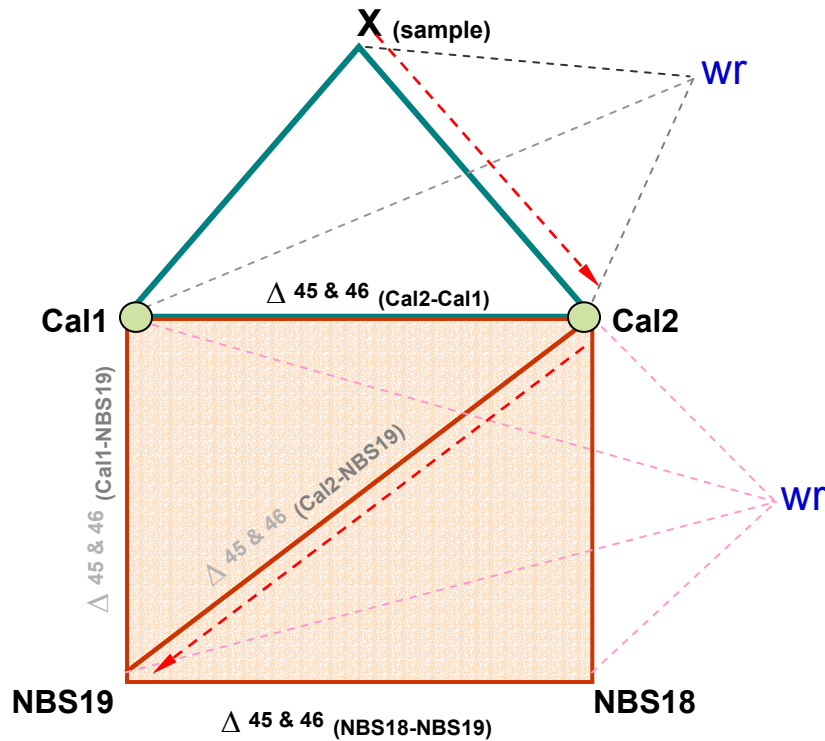
$$\begin{aligned} R_{\text{Sam}}/R_{\text{VPDBC}^{18}\text{O}_2} &= [R_{\text{Sam}}/R_{\text{W-Ref}}] * [1/(R_{\text{LStd}}/R_{\text{W-Ref}})] * (R_{\text{Link-Std}}/R_{\text{VPDBC}^{18}\text{O}_2}) \\ &= [\Delta_{\text{Sam-LStd}} * 10^{-3} + 1] * [\Delta_{\text{LStd-NBS19CO}_2} * 10^3 + 1] * (R_{\text{NBS19CO}_2}/R_{\text{VPDBC}^{18}\text{O}_2}) \end{aligned}$$

where  $(R_{\text{Sam}}/R_{\text{W-Ref}})$  from daily measurements,  
 $(R_{\text{LinkStd}}/R_{\text{VPDBC}^{18}\text{O}_2})$  from annual calibrations,  
 $R_{\text{LinkStd}}$  is the link between calibrations and daily measurements,  
Both Cal1 and Cal2 are  $R_{\text{LinkStd}}$  in our lab)  
 $(R_{\text{NBS19}}/R_{\text{VPDBC}^{18}\text{O}_2})$  from IAEA assigned value

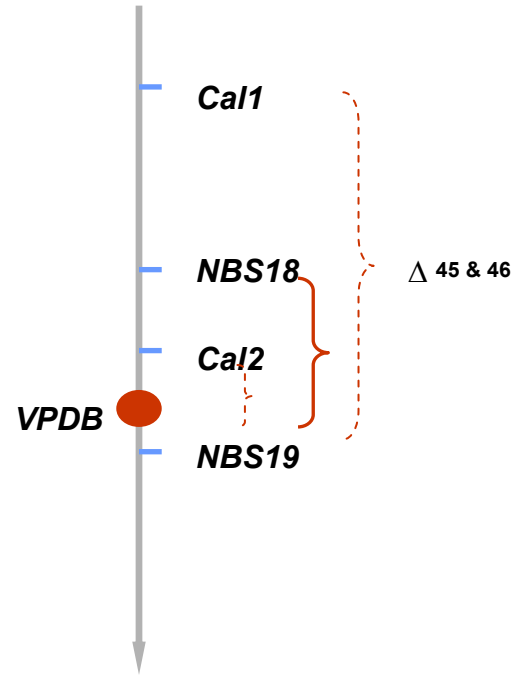
$$\text{Big Delta } (R^{45 \text{ or } 46} \text{ or } R^{13 \text{ or } 18}): \Delta_{\text{A-B}} = [(R_{\text{A}} - R_{\text{B}})/R_{\text{B}}] * 10^3 = (\delta_{\text{A-ref}} - \delta_{\text{B-ref}}) / (\delta_{\text{B-ref}} * 10^{-3} + 1)$$

which is independent on references

# Schematic of Multi-Carbonates Direct Link (MCDL) in Isotope Measurements at the Stable Isotope Research Lab, ASTD/STB/EC, Toronto, Canada



Annual calibration   
 Daily measurement   
 Traceability path



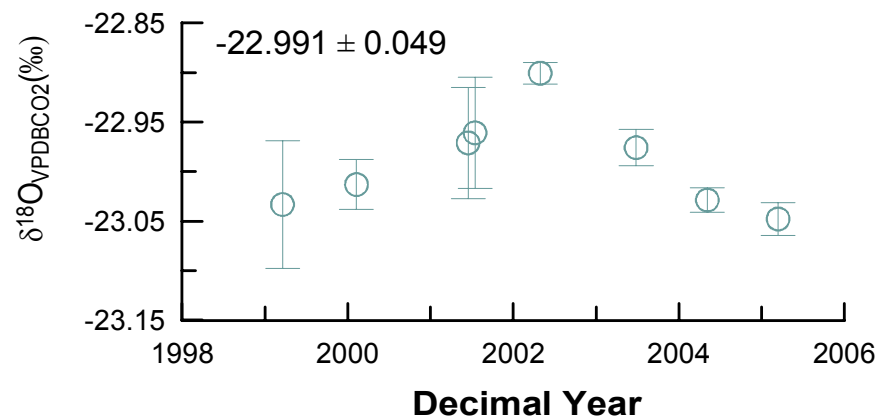
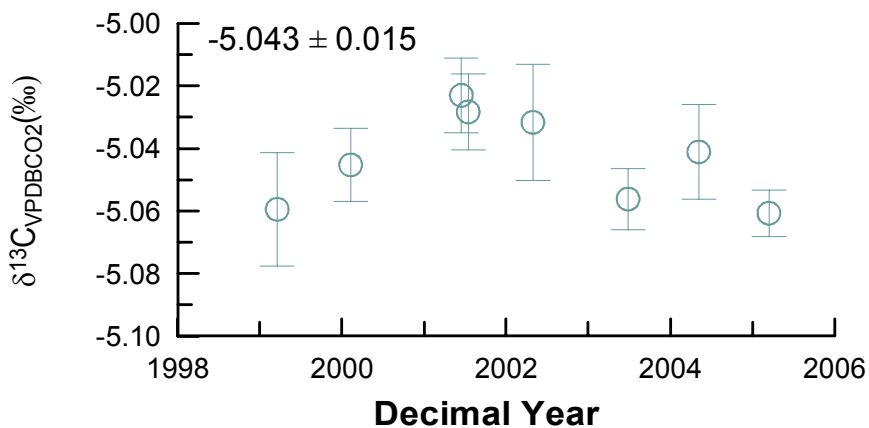
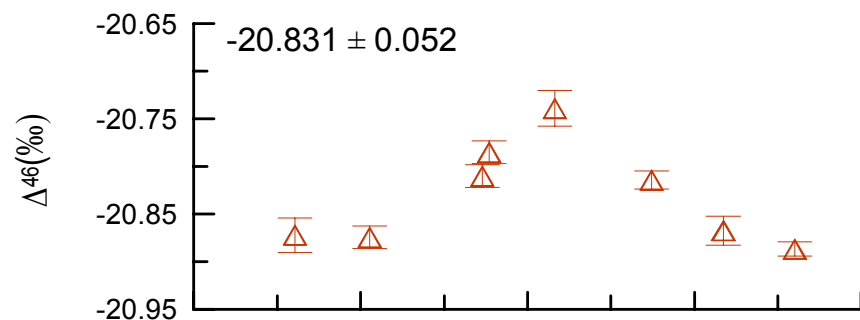
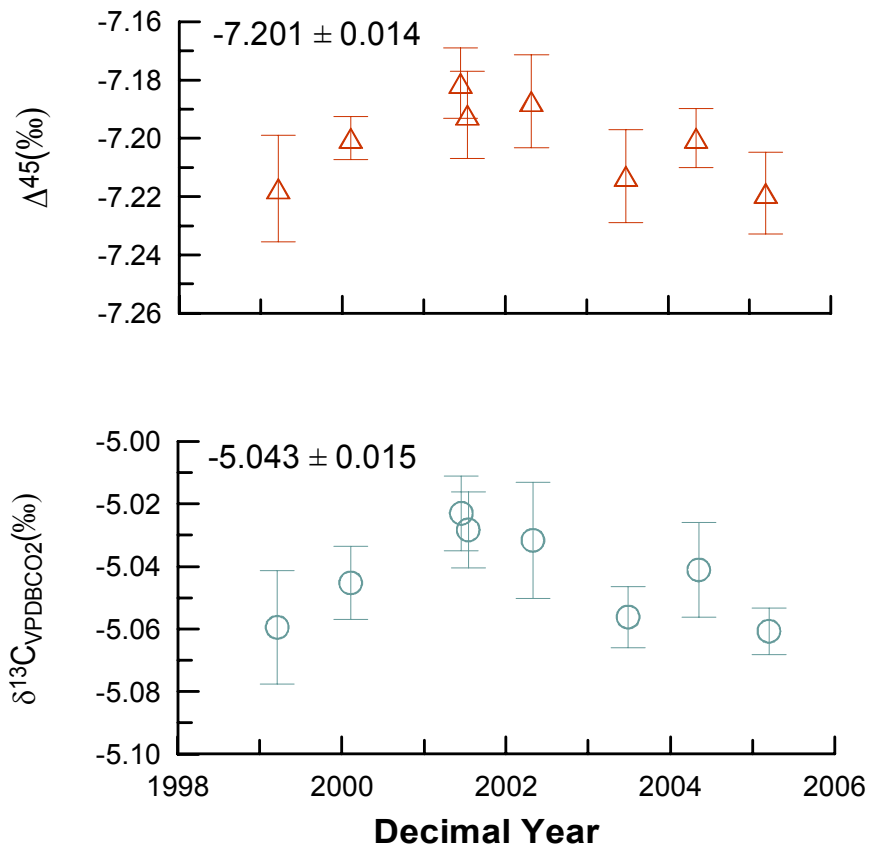
$$\Delta_{45 \& 46} (A-B) = [(R_A - R_B)/R_B] * 10^3$$

$$= (\delta_{A-ref} - \delta_{B-ref}) / (\delta_{B-ref} * 10^{-3} + 1)$$

**Note:**

- Cal1 & Cal2 are the lab calcium carbonate standards in the isotope lab, ASTD/ STB/EC;
- Big Delta values (i.e.  $\Delta^{45 \& 46}$ ) are independent on working reference (Wr) gases and should be precisely determined by IRMS;
- $\delta^{13}C$  and  $\delta^{18}O$  will be dependent on  $\Delta^{45 \& 46}$ .

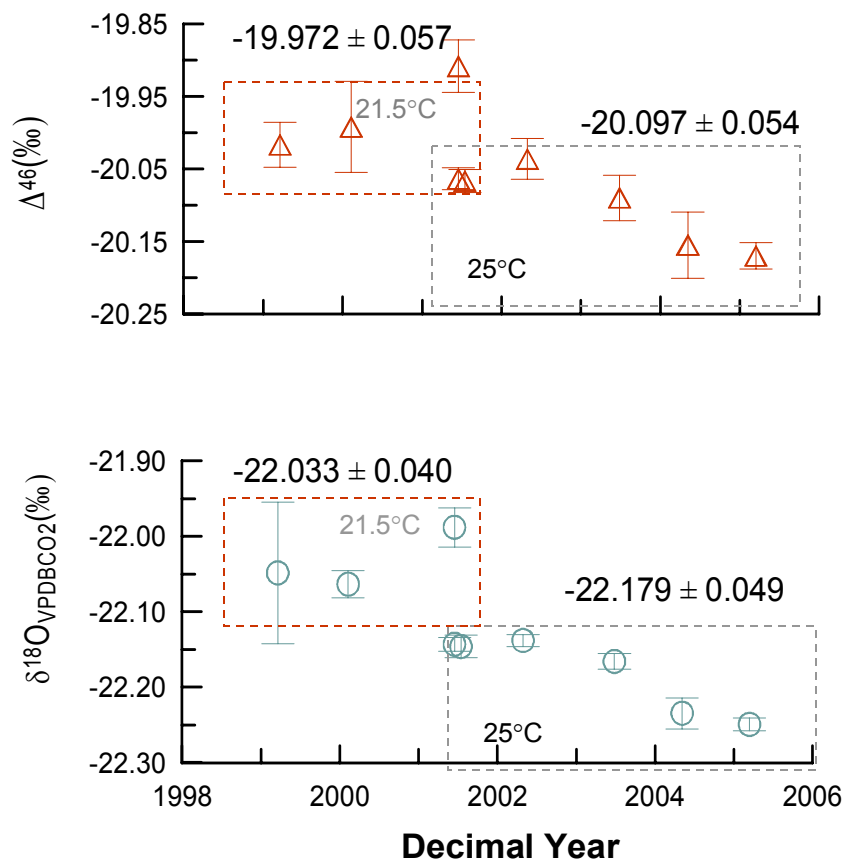
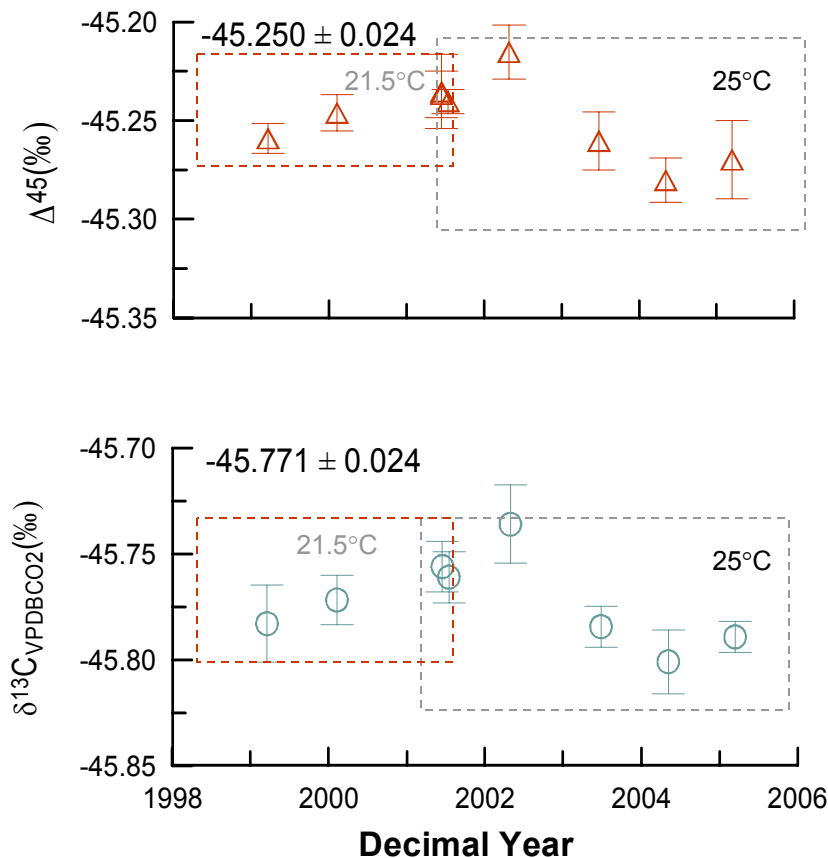
# Isotopic Compositions in NBS18\* directly calibrated by NBS19



## Note:

- both NBS19 and NBS18 were reacted with 100 %  $\text{H}_3\text{PO}_4$  (density: **1.91-1.92**) at **25°C**;
- each data point represents the average value of > three (i.e. 3-8) individual reactions) with **one**  $\sigma$  Std.
- The numbers shown on each plot represents the average of multi year calibrations with one  $\sigma$  Std at **25°C**.

# Isotopic Compositions in Cal1\* directly calibrated by NBS19



## Note:

- NBS19 was reacted with 100 % H<sub>3</sub>PO<sub>4</sub> at 25°C always;
- \*Cal1 were reacted with 100 % H<sub>3</sub>PO<sub>4</sub> at two different temperatures, i.e. 21.5°C and 25°C
- each data point represents the average value of > **three** (i.e. 3-8) individual reactions with **one**  $\sigma$  Std.
- The numbers shown on each plot represents the average of multi year calibrations with one  $\sigma$  Std at either 21.5°C or 25°C. and the average values for carbon isotope include all the data from both 21.5°C and 25°C.

