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How accurately do we know $^{13}\text{C}/^{12}\text{C}$, $^{18}\text{C}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ ratios in CO_2 and their corresponding δ values?

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Recommended inter-laboratory comparability (1σ)

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- ✦ CO_2 ± 0.1 ppm (± 0.05 ppm in southern hemisphere)
- ✦ $^{13}\delta(\text{CO}_2)$ ± 0.01 ‰
- ✦ $^{18}\delta(\text{CO}_2)$ ± 0.05 ‰

How do we measure carbon and oxygen isotope ratios with mass spectrometers?

Measure ion current ratios of sample relative to reference
(NBS 19-CO₂ as stand-in for VPDB-CO₂)

m/z 44 $^{12}\text{C}^{16}\text{O}_2^+$

m/z 45 $^{13}\text{C}^{16}\text{O}_2^+$ $^{12}\text{C}^{17}\text{O}^{16}\text{O}^+$

m/z 46 $^{12}\text{C}^{18}\text{O}^{16}\text{O}^+$ $^{13}\text{C}^{17}\text{O}^{16}\text{O}^+$ $^{12}\text{C}^{17}\text{O}_2^+$

$$^{45}\delta_I = \frac{^{45}I / ^{44}I}{^{45}I_r / ^{44}I_r} - 1$$

We **assume** that all minor isotopologues have the same relative ionisation efficiency. Then, the ion current delta is the same as the isotopologue delta.

$$^{45}\delta_I = ^{45}\delta = \frac{^{45}R / ^{44}R}{^{45}R_r / ^{44}R_r} - 1$$

"Conventional" isobaric correction using isotopologue and isotope ratios R

$${}^{45}\delta = \frac{{}^{45}R/{}^{44}R}{{}^{45}R_r/{}^{44}R_r} - 1$$

$${}^{45}R = {}^{13}R + 2{}^{17}R$$

$${}^{45}R_r = {}^{13}R_r + 2{}^{17}R_r$$

$${}^{46}R = 2{}^{18}R + 2{}^{13}R{}^{17}R + {}^{17}R^2$$

$${}^{46}R_r = 2{}^{18}R_r + 2{}^{13}R_r{}^{17}R_r + {}^{17}R_r^2$$

$${}^{17}R = A{}^{18}R^{0.528}$$

$${}^{17}R_r = A{}^{18}R_r^{0.528}$$

Solve for 3 unknowns ${}^{13}R$, ${}^{17}R$, ${}^{18}R$

"New" isobaric correction using δ values (Kaiser & Röckmann 2008)

$$^{13}\delta = \frac{^{13}R}{^{13}R_r} - 1 \quad ^{17}\delta = \frac{^{17}R}{^{17}R_r} - 1 \quad ^{18}\delta = \frac{^{18}R}{^{18}R_r} - 1$$

$$^{45}R_r \ ^{45}\delta = ^{13}R_r \ ^{13}\delta + 2^{17}R_r \ ^{17}\delta$$

$$^{46}R_r \ ^{46}\delta = 2^{18}R_r \ ^{18}\delta + 2^{13}R_r \ ^{17}R_r (^{13}\delta + ^{17}\delta + ^{13}\delta^{17}\delta) + ^{17}R_r^2 (2^{17}\delta + ^{17}\delta^2)$$

$$^{17}\delta = (1 + ^{17}\Delta)(1 + ^{18}\delta)^{0.528} - 1$$

Solve for 3 unknowns $^{13}\delta$, $^{18}\delta$, $^{17}\delta$

(including possible ^{17}O isotope excess aka oxygen isotope anomalies)

"New" isobaric correction using δ values (Kaiser & Röckmann 2008)

$$^{13}\delta = ^{45}\delta + 2C(^{45}\delta - ^{17}\delta)$$

$$^{18}\delta = ^{46}\delta + D\left[(2 + C)^{46}\delta - (2 - 2C)^{17}\delta - (2 + 4C)^{45}\delta(1 + ^{17}\delta) + 3C^{17}\delta^2\right]$$

$$^{17}\delta = (1 + ^{17}\Delta)(1 + ^{18}\delta)^{0.528} - 1$$

$$C = \frac{^{17}R_r}{^{13}R_r} \quad D = \frac{^{13}R_r ^{17}R_r}{2^{18}R_r}$$

⇒ no isotope ratios required for δ calculation

How to measure C (and D)?

See also Poster P10

C from δ measurements only

$$\frac{{}^{17}R_{\text{VSMOW}}}{{}^{13}R_{\text{VPDB-CO}_2}} = \frac{(1 + {}^{13}\delta_{\text{NBS19-CO}_2/\text{VPDB-CO}_2})/2}{\frac{{}^{17}\delta_{\text{H}_2^{16}\text{O}/\text{VSMOW}}^{\text{normalised}} (1 + {}^{45}\delta_{\text{NBS19-CO}_2/\text{w}})}{{}^{45}\delta_{\text{H}_2^{16}\text{O-CO}_2/\text{w}} - {}^{45}\delta_{\text{VSMOW-CO}_2/\text{w}}} - 1 - {}^{17}\delta_{\text{NBS19-CO}_2/\text{VSMOW}}$$

derived from Li et al. 1988

$$\frac{{}^{17}R_{\text{VSMOW}}}{{}^{13}R_{\text{VPDB-CO}_2}} = \frac{(1 + {}^{13}\delta_{\text{NBS19-CO}_2/\text{VPDB-CO}_2})/2}{\frac{{}^{17}\delta_{^{16}\text{O}_2/\text{w-O}_2} (1 + {}^{17}\delta_{\text{w-O}_2/\text{VSMOW}}) (1 + {}^{45}\delta_{\text{NBS19-CO}_2/\text{w}})}{{}^{45}\delta_{^{16}\text{O}_2\text{-CO}_2/\text{w}} - {}^{45}\delta_{\text{w-O}_2\text{-CO}_2/\text{w}}} - 1 - {}^{17}\delta_{\text{NBS19-CO}_2/\text{VSMOW}}$$

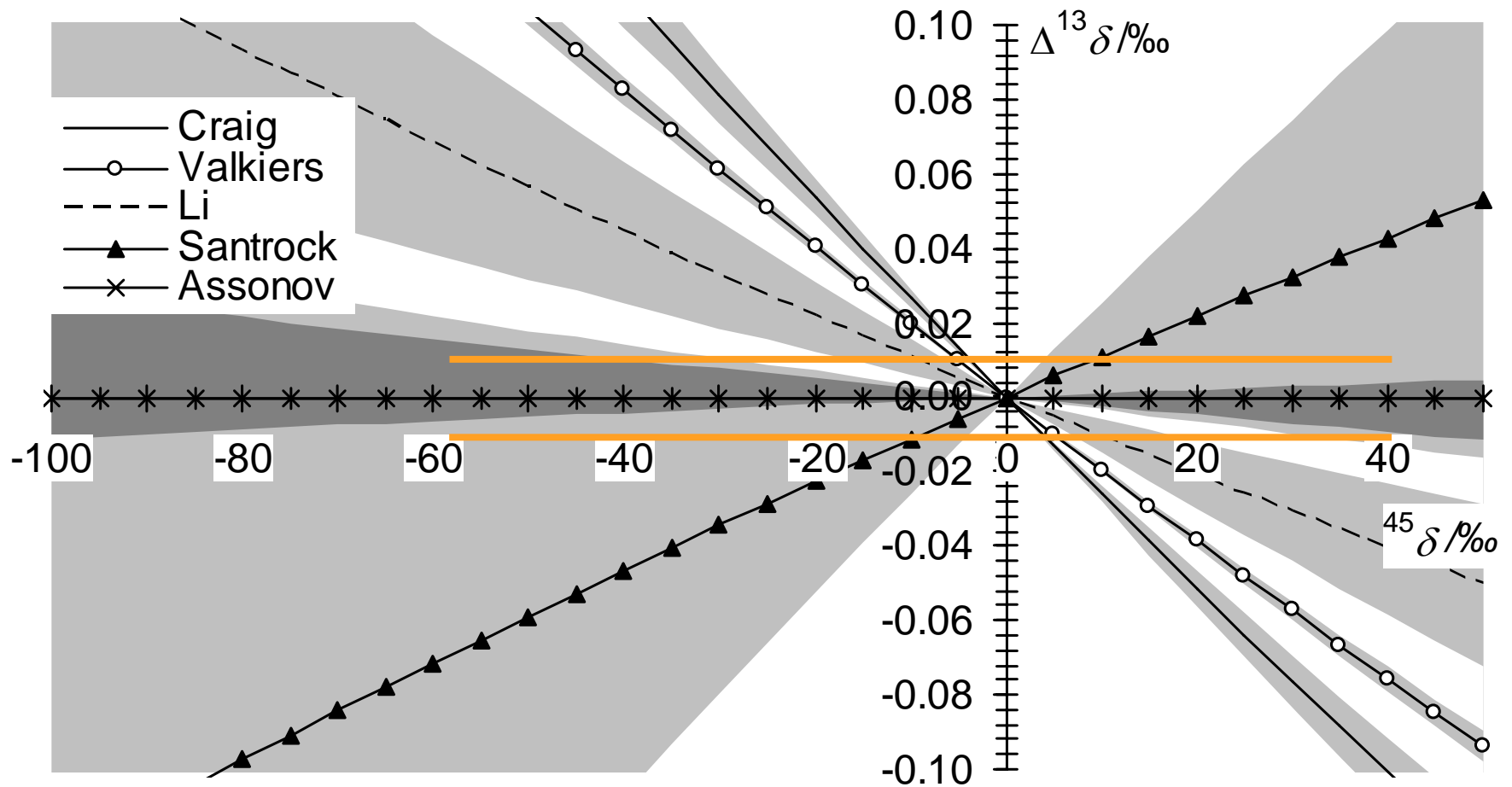
derived from Assonov & Brenninkmeijer 2003

Values for the ratio $^{17}R/^{13}R$ for VPDB-CO₂

orange: derived from δ measurements only

$10^3 C$	Reference
33.8±0.1	Craig (1957)
35.7±0.7	Santrock et al. (1985)
34.6±0.2	Li et al. (1988)
35.16±0.05	Assonov & Brenninkmeijer (2003)
34.17±0.04	Valkiers et al. (2007)

Influence of C on the computed $^{13}\delta$ value



Influence of $^{17}\Delta$ on the computed $^{13}\delta$ value

$$^{17}\delta = (1 + ^{17}\Delta)(1 + ^{18}\delta)^{0.528} - 1 \approx ^{17}\Delta + 0.528^{18}\delta + \dots$$

$$^{13}\delta = (1 + 2C)^{45}\delta - 2C^{17}\delta$$

$$\approx (1 + 2C)^{45}\delta - 0.528 \times 2C^{18}\delta - 2C^{17}\Delta$$

$$\approx 1.0703^{45}\delta - 0.0371^{18}\delta - 0.0703^{17}\Delta$$

$$^{17}\Delta(\text{atm. O}_2) = -0.25 \text{ ‰ (Barkan \& Luz 2000)}$$

$$^{17}\Delta(\text{trop. CO}_2) = +0.65 \text{ ‰ (Hoag et al. 2005)}$$

This could lead to systematic offsets in $^{13}\delta$ between -0.05 and 0.02 ‰, depending on CO_2 source.

Influence of the relative ionisation efficiency of $^{12}\text{C}^{17}\text{O}^{16}\text{O}$ versus $^{13}\text{C}^{16}\text{O}_2$

Assume $^{13}\delta = -10\text{‰}$, $^{18}\delta = 40\text{‰}$ and $^{17}\Delta = 0\text{‰}$.

Relative difference in ionisation efficiency	$^{45}\delta / \text{‰}$
0	-7.968
0.001	-7.966
0.01	-7.949
0.1	-7.772

How good is the assumption that relative ionisation efficiencies are the same?

14th WMO/IAEA CO₂ Experts Meeting (2007)

accuracy

closeness of agreement between a test result and the accepted **reference value** (VIM 2nd edition, 1993).

VIM 3rd edition (2008)

measurement **accuracy** (2.13)

closeness of agreement between a measured quantity value and a **true quantity value** of a measurand

measurement **trueness** (2.14)

closeness of agreement between the average of an infinite number of replicate measured quantity values and a **reference quantity value** (5.18)

VIM 3rd edition (2008)

reference quantity value

reference value

quantity value used as a basis for comparison with values of quantities of the same kind

NOTE 1 A reference quantity value can be a **true quantity value** of a measurand, in which case it is unknown, or a **conventional quantity value**, in which case it is known.

Can secondary reference materials improve this situation?

Scale normalisation with
L-SVEC (Li_2CO_3) $^{13}\delta = -46.6 \text{ ‰}$
(Coplen et al. 2006)

I *think* this is a conventional reference value.
Not a true one.
Nevertheless, it does improve our trueness.
But not necessarily the accuracy.

$^{13}R(\text{VPDB-CO}_2)$

$10^6 \text{ }^{13}R$ Original ($\pm 1 \sigma$)		References
11237.2		Craig (1957); Nier (1950)

IAEA Recommendation

$^{13}R(\text{VPDB-CO}_2)$

$10^6 \ ^{13}R$ Original ($\pm 1 \sigma$)	$10^6 \ ^{13}R$ Re-evaluated (Kaiser, 2008)	References
11237.2 \pm 30	11232.3 \pm 39	Craig (1957); Nier (1950)

$^{13}R(\text{VPDB-CO}_2)$

$10^6 \ ^{13}R$ Original ($\pm 1 \sigma$)	$10^6 \ ^{13}R$ Re-evaluated (Kaiser, 2008)	References
11237.2 \pm 30	11232.3 \pm 39	Craig (1957); Nier (1950)
11179.7 \pm 28	11182.4 \pm 16	Chang & Li (1990)
	11090.1 \pm 6	Nørgaard et al. (1999)
11101.4 \pm 9	11086.4 \pm 3	Russe et al. (2004); Coplen et al. (2006)
11137.6 \pm 1.6	11137.6 \pm 1.6	Valkiers et al. (2007)

Average of last 4 values: $(11124 \pm 45) \times 10^{-6}$

$^{18}R(\text{VPDB-CO}_2)$

$10^6 \text{ }^{18}R$ Original ($\pm 1 \sigma$)		References
2088.35		Baertschi et al. (1976); O'Neil et al. (1975)

IAEA Recommendation

$^{18}R(\text{VPDB-CO}_2)$

$10^6 \text{ }^{18}R$ Original ($\pm 1 \sigma$)	$10^6 \text{ }^{18}R$ Re-evaluated (Kaiser, 2008)	References
2088.35 \pm 0.80	2089.32 \pm 1.5	Baertschi et al. (1976); O'Neil et al. (1975)

Recommendation (IAEA, 1995)

$$^{18}\delta_{\text{VPDB-CO}_2/\text{VSMOW}} = 41.47 \text{ ‰ (with } ^{18}\delta_{\text{SLAP}/\text{VSMOW}} = -55.5 \text{ ‰)}$$

Re-evaluated (Kaiser, 2008)

$$^{18}\delta_{\text{VPDB-CO}_2/\text{VSMOW}} = (42.0 \pm 0.7) \text{ ‰ (with } ^{18}\delta_{\text{SLAP}/\text{VSMOW}} = -56.18 \text{ ‰)}$$

$^{18}R(\text{VPDB-CO}_2)$

$10^6 \text{ }^{18}R$ Original ($\pm 1 \sigma$)	$10^6 \text{ }^{18}R$ Re-evaluated (Kaiser, 2008)	References
2088.35 \pm 0.80	2089.32 \pm 1.5	Baertschi et al. (1976); O'Neil et al. (1975)
2079.00 \pm 2.5	2078.71 \pm 2.5	Craig (1957); Nier (1950)
	2107.69 \pm 2.4	Valkiers & De Bièvre (1993)
	2087.54 \pm 1.6	Nørgaard et al. (1999)
2088.24 \pm 0.48	2088.24 \pm 0.48	Valkiers et al. (2007)

Average of rows 3, 5 & 6: $(2088.37 \pm 0.90) \times 10^{-6}$

$^{17}R(\text{VPDB-CO}_2)$

$10^6 \ ^{17}R$ Original ($\pm 1 \sigma$)		References
395.11 \pm 0.94		Assonov & Brenninkmeijer (1993); Craig (1957)

IAEA Recommendation

$^{17}R(\text{VPDB-CO}_2)$

$10^6 \text{ }^{18}R$ Original ($\pm 1 \sigma$)	$10^6 \text{ }^{18}R$ Re-evaluated (Kaiser, 2008)	References
(395.11 \pm 0.94)	(395.11 \pm 1.66)	Assonov & Brenninkmeijer (1993); Craig (1957)

$^{17}R(\text{VPDB-CO}_2)$

$10^6 \text{ }^{18}R$ Original ($\pm 1 \sigma$)	$10^6 \text{ }^{18}R$ Re-evaluated (Kaiser, 2008)	References
(395.11 \pm 0.94)	(395.11 \pm 1.66)	Assonov & Brenninkmeijer (1993); Craig (1957)
379.95 \pm 0.5	380.18 \pm 0.2	Craig (1957); Nier (1950)
	394.67 \pm 2	Valkiers & De Bièvre (1993)
	(389.88 \pm 0.2)	Nørgaard et al. (1999); Assonov & Brenninkmeijer (1993)
380.58 \pm 0.48	380.58 \pm 0.48	Valkiers et al. (2007)

Why should we care about R ?

- ✦ Nice to know ...
- ✦ To make isotope measurements SI traceable
[but: precision of R always worse than δ]
- ✦ To cross-check with data-reduction coefficients from other molecules (O_2 , CO , N_2O , SO_2)
[B , C , D , E , F , (G , H , I) – see poster P10]
- ✦ To allow calculation of isotopologue mixing ratios

Calculation of isotopologue mixing ratios

$$x(^{12}\text{C}^{16}\text{O}_2) = \frac{x(\text{CO}_2)}{(1+^{13}R)(1+^{17}R+^{18}R)}$$

$$x(\text{CO}_2) = 390 \text{ } \mu\text{mol/mol}$$

$$^{18}R = 2089.3 \times 10^{-6}$$

$$C = 0.03516$$

$$^{13}R = 11237.2 \times 10^{-6}$$

$$x(^{12}\text{C}^{16}\text{O}_2) = 383.76 \text{ } \mu\text{mol/mol}$$

$$^{13}R = 11086.4 \times 10^{-6}$$

$$x(^{12}\text{C}^{16}\text{O}_2) = 383.82 \text{ } \mu\text{mol/mol}$$

$$\Delta x = 0.06 \text{ } \mu\text{mol/mol}$$

Is this important? You decide ...

Conclusions

- ✦ Agreed isobaric correction and normalisation schemes improve reproducibility (and maybe trueness) of δ values.
- ✦ Several minor issues remain for the accuracy of δ values
 - ✦ confirmation of C (and D)
 - ✦ $^{17}\Delta$ value of tropospheric CO_2
 - ✦ relative ionisation efficiency of $^{12}\text{C}^{17}\text{O}^{16}\text{O}$
- ✦ Major issues remain for the accuracy of R values
 - ✦ $^{13}R(\text{VPDB-}\text{CO}_2)$: converging?
 - ✦ $^{18}R(\text{VPDB-}\text{CO}_2)$: converged
 - ✦ $^{17}R(\text{VPDB-}\text{CO}_2)$: diverging [but can be linked to ^{13}R]