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 $\text{CO}_2$ and their corresponding $\delta$ values?

Jan Kaiser

School of Environmental Sciences
University of East Anglia
Norwich
United Kingdom
Recommended inter-laboratory comparability ($1\sigma$)

14th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques, 10-13 September 2007 in Helsinki, Finland

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

\[
\begin{align*}
&m/z 44 \quad ^{12}\text{C}^{16}\text{O}_2^+ \\
&m/z 45 \quad ^{13}\text{C}^{16}\text{O}_2^+ \quad ^{12}\text{C}^{17}\text{O}^{16}\text{O}^+ \\
&m/z 46 \quad ^{12}\text{C}^{18}\text{O}^{16}\text{O}^+ \quad ^{13}\text{C}^{17}\text{O}^{16}\text{O}^+ \quad ^{12}\text{C}^{17}\text{O}_2^+
\end{align*}
\]

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

\[
45 \delta_l = \frac{45 \text{I}_l / 44 \text{I}_l}{45 \text{I}_r / 44 \text{I}_r} - 1
\]

\[
45 \delta_l = 45 \delta = \frac{45 R / 44 R}{45 R_r / 44 R_r} - 1
\]
"Conventional" isobaric correction using isotopologue and isotope ratios $R$

\[ 45\delta = \frac{45R/44R}{45R_r/44R_r} - 1 \]

\[
\begin{align*}
45R &= 13R + 2^{17}R \\
46R &= 2^{18}R + 2^{13}R^{17}R + 17R^2 \\
17R &= A^{18}R^{0.528}
\end{align*}
\]

\[
\begin{align*}
45R_r &= 13R_r + 2^{17}R_r \\
46R_r &= 2^{18}R_r + 2^{13}R_r^{17}R_r + 17R_r^2 \\
17R_r &= A^{18}R_r^{0.528}
\end{align*}
\]

Solve for 3 unknowns $^{13}R$, $^{17}R$, $^{18}R$
"New" isobaric correction using $\delta$ values (Kaiser & Röckmann 2008)

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

$$
45\delta = \frac{13R}{13R_r} \cdot 13\delta + 2 \cdot \frac{17R}{17R_r} \cdot 17\delta
$$

$$
46\delta = 2 \cdot \frac{18R}{18R_r} \cdot 18\delta + 2 \cdot \frac{13R}{18R_r} \cdot 17\delta + 2 \cdot \frac{13R}{18R_r} \cdot 17\delta + 17\delta \cdot 17\delta + 2 \cdot \frac{17R}{18R_r} \cdot 17\delta + 2 \cdot \frac{17R}{18R_r} \cdot 17\delta
$$

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

Solve for 3 unknowns $13\delta$, $18\delta$, $17\delta$
(including possible $17^O$ isotope excess aka oxygen isotope anomalies)
"New" isobaric correction using $\delta$ values (Kaiser & Röckmann 2008)

\[13 \delta = 45 \delta + 2C(45 \delta - 17 \delta)\]
\[18 \delta = 46 \delta + D[(2 + C)46 \delta - (2 - 2C)17 \delta - (2 + 4C)45 \delta(1+17 \delta) + 3C17 \delta^2]\]
\[17 \delta = (1+17 \Delta)(1+18 \delta)^{0.528} - 1\]

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

⇒ no isotope ratios required for $\delta$ calculation

How to measure C (and D)?

See also Poster P10
C from δ measurements only

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

derived from Li et al. 1988

\[
\frac{^{17}R_{\text{VSMOW}}}{^{13}R_{\text{VPDB-CO}_2}} = \frac{(1+^{13}\delta_{\text{NBS19-CO}_2/\text{VPDB-CO}_2})/2}{\frac{^{17}\delta_{\text{O}_2/w-O_2}}{^{45}\delta_{\text{O}_2-CO}_2/w} - \frac{^{45}\delta_{\text{w-O}_2-CO}_2/w}{1-^{17}\delta_{\text{NBS19-CO}_2/\text{VSMOW}}}}
\]

derived from Assonov & Brenninkmeijer 2003
Values for the ratio $^{17}R/^{13}R$ for VPDB-CO$_2$

orange: derived from $\delta$ measurements only

<table>
<thead>
<tr>
<th>$10^3$ C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>33.8±0.1</td>
<td>Craig (1957)</td>
</tr>
<tr>
<td>35.7±0.7</td>
<td>Santrock et al. (1985)</td>
</tr>
<tr>
<td>34.6±0.2</td>
<td>Li et al. (1988)</td>
</tr>
<tr>
<td>35.16±0.05</td>
<td>Assonov &amp; Brenninkmeijer (2003)</td>
</tr>
<tr>
<td>34.17±0.04</td>
<td>Valkiers et al. (2007)</td>
</tr>
</tbody>
</table>
Influence of $C$ on the computed $^{13}\delta$ value
Influence of $^{17}\Delta$ on the computed $^{13}\delta$ value

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

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

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

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

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

$^{17}\Delta$(trop. CO$_2$) = +0.65 ‰ (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 $^{13}\delta = -10 \, \%$, $^{18}\delta = 40 \, \%$ and $^{17}\Delta = 0 \, \%$.

<table>
<thead>
<tr>
<th>Relative difference in ionisation efficiency</th>
<th>$^{45}\delta / %$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$-7.968$</td>
</tr>
<tr>
<td>0.001</td>
<td>$-7.966$</td>
</tr>
<tr>
<td>0.01</td>
<td>$-7.949$</td>
</tr>
<tr>
<td>0.1</td>
<td>$-7.772$</td>
</tr>
</tbody>
</table>

How good is the assumption that relative ionisation efficiencies are the same?
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 3\textsuperscript{rd} edition (2008)

reference quantity value
reference value

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

\textbf{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$_2$CO$_3$) $^{13}\delta = -46.6$ \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.
\[ ^{13}R(\text{VPDB-CO}_2) \]

<table>
<thead>
<tr>
<th>(10^6 \times ^{13}R)</th>
<th>Original (±1σ)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>11237.2</td>
<td></td>
<td>Craig (1957); Nier (1950)</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>$10^6 , ^{13}R$</th>
<th>$10^6 , ^{13}R$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original ($\pm 1\sigma$)</td>
<td>Re-evaluated (Kaiser, 2008)</td>
<td>Craig (1957); Nier (1950)</td>
</tr>
<tr>
<td>11237.2±30</td>
<td>11232.3±39</td>
<td></td>
</tr>
</tbody>
</table>
$$^{13}R(\text{VPDB-CO}_2)$$

<table>
<thead>
<tr>
<th>10^6 13R</th>
<th>10^6 13R</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original (±1σ)</td>
<td>Re-evaluated (Kaiser, 2008)</td>
<td></td>
</tr>
<tr>
<td>11237.2±30</td>
<td>11232.3±39</td>
<td>Craig (1957); Nier (1950)</td>
</tr>
<tr>
<td>11179.7±28</td>
<td>11182.4±16</td>
<td>Chang &amp; Li (1990)</td>
</tr>
<tr>
<td></td>
<td>11090.1±6</td>
<td>Nørgaard et al. (1999)</td>
</tr>
<tr>
<td>11101.4±9</td>
<td>11086.4±3</td>
<td>Russe et al. (2004); Coplen et al. (2006)</td>
</tr>
<tr>
<td>11137.6±1.6</td>
<td>11137.6±1.6</td>
<td>Valkiers et al. (2007)</td>
</tr>
</tbody>
</table>

Average of last 4 values: (11124±45) × 10^-6
<table>
<thead>
<tr>
<th>$10^6 \text{ } ^{18}R$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original (±1σ)</td>
<td>Baertschi et al. (1976); O’Neil et al. (1975)</td>
</tr>
<tr>
<td>2088.35</td>
<td></td>
</tr>
</tbody>
</table>

IAEA Recommendation
\[ ^{18}R_{\text{VPDB-CO}_2} \]

<table>
<thead>
<tr>
<th>(10^6 , ^{18}R)</th>
<th>(10^6 , ^{18}R)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original (±1σ)</td>
<td>Re-evaluated (Kaiser, 2008)</td>
<td>Baertschi et al. (1976); O’Neil et al. (1975)</td>
</tr>
<tr>
<td>2088.35±0.80</td>
<td>2089.32±1.5</td>
<td></td>
</tr>
</tbody>
</table>

Recommendation (IAEA, 1995)

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

Re-evaluated (Kaiser, 2008)

\[ ^{18}\delta_{\text{VPDB-CO}_2/\text{VSMOW}} = \) (42.0±0.7) ‰ \( \) (with \( ^{18}\delta_{\text{SLAP/VSMOW}} = \) –56.18 ‰)
### $^{18}R$ (VPDB-CO$_2$)

<table>
<thead>
<tr>
<th>$10^6$ $^{18}R$</th>
<th>$10^6$ $^{18}R$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Original (±1σ)</strong></td>
<td><strong>Re-evaluated</strong> (Kaiser, 2008)</td>
<td></td>
</tr>
<tr>
<td>2088.35±0.80</td>
<td>2089.32±1.5</td>
<td>Baertschi et al. (1976); O’Neil et al. (1975)</td>
</tr>
<tr>
<td>2079.00±2.5</td>
<td>2078.71±2.5</td>
<td>Craig (1957); Nier (1950)</td>
</tr>
<tr>
<td>2107.69±2.4</td>
<td></td>
<td>Valkiers &amp; De Bièvre (1993)</td>
</tr>
<tr>
<td>2087.54±1.6</td>
<td></td>
<td>Nørgaard et al. (1999)</td>
</tr>
<tr>
<td>2088.24±0.48</td>
<td>2088.24±0.48</td>
<td>Valkiers et al. (2007)</td>
</tr>
</tbody>
</table>

Average of rows 3, 5 & 6: $(2088.37±0.90) \times 10^{-6}$
<table>
<thead>
<tr>
<th>$10^6 \ 17R$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original (±1σ)</td>
<td>Assonov &amp; Brenninkmeijer (1993); Craig (1957)</td>
</tr>
<tr>
<td>395.11±0.94</td>
<td></td>
</tr>
</tbody>
</table>

**IAEA Recommendation**
### $^{17}R_{(VPDB-CO_2)}$

<table>
<thead>
<tr>
<th>$10^6 \ 18R$</th>
<th>$10^6 \ 18R$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original (±1σ)</td>
<td>Re-evaluated (Kaiser, 2008)</td>
<td>Assonov &amp; Brenninkmeijer (1993); Craig (1957)</td>
</tr>
<tr>
<td>$(395.11±0.94)$</td>
<td>$(395.11±1.66)$</td>
<td></td>
</tr>
</tbody>
</table>

References:
- Assonov & Brenninkmeijer (1993);
- Craig (1957)
### $^{17}R_{\text{VPDB-CO}_2}$

<table>
<thead>
<tr>
<th>$10^6$ $^{18}R$</th>
<th>$10^6$ $^{18}R$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original (±1σ)</td>
<td>Re-evaluated (Kaiser, 2008)</td>
<td></td>
</tr>
<tr>
<td>(395.11±0.94)</td>
<td>(395.11±1.66)</td>
<td>Assonov &amp; Brenninkmeijer (1993); Craig (1957)</td>
</tr>
<tr>
<td>379.95±0.5</td>
<td>380.18±0.2</td>
<td>Craig (1957); Nier (1950)</td>
</tr>
<tr>
<td></td>
<td>394.67±2</td>
<td>Valkiers &amp; De Bièvre (1993)</td>
</tr>
<tr>
<td></td>
<td>(389.88±0.2)</td>
<td>Nørgaard et al. (1999); Assonov &amp; Brenninkmeijer (1993)</td>
</tr>
<tr>
<td>380.58±0.48</td>
<td>380.58±0.48</td>
<td>Valkiers et al. (2007)</td>
</tr>
</tbody>
</table>
Why should we care about $R$?

- Nice to know …
- To make isotope measurements SI traceable
  [but: precision of $R$ always worse than $\delta$]
- 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 callow calculation of isotopologue mixing ratios
Calculation of isotopologue mixing ratios

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

\[ x(\text{CO}_2) = 390 \ \mu\text{mol/mol} \]
\[ ^{18}R = 2089.3 \times 10^{-6} \]
\[ C = 0.03516 \]

\[ ^{13}R = 11237.2 \times 10^{-6} \]
\[ x(^{12}\text{C}^{16}\text{O}_2) = 383.76 \ \mu\text{mol/mol} \]

\[ ^{13}R = 11086.4 \times 10^{-6} \]
\[ x(^{12}\text{C}^{16}\text{O}_2) = 383.82 \ \mu\text{mol/mol} \]

\[ \Delta x = 0.06 \ \mu\text{mol/mol} \]

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
  - \(^{13}R(\text{VPDB-CO}_2)\): converging?
  - \(^{18}R(\text{VPDB-CO}_2)\): converged
  - \(^{17}R(\text{VPDB-CO}_2)\): diverging [but can be linked to \(^{13}R\)]