The IAEA carbonate reference materials aimed at the VPDB scale realization with low uncertainty

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IAEA - custodian of primary Reference Materials (RMs):

• **Primary standards (artefacts)** are used to establish the entire calibration schemes for stable isotopes, similar to prototypes of *kilogram* and *meter*. Example: VSMOW & SLAP.

• Realizations of these standards – **highest-level RMs (so-called primary RMs)** are distributed by the IAEA.

• When exhausted, primary RMs need to be replaced. Still, primary RMs have the lowest possible uncertainty.
  Examples: VSMOW => VSMOW2, NBS19 => IAEA-603.

• Secondary RMs are characterised directly against primary RMs.

Primary RMs have a similar status as the *kilogram prototype* and its official copies (before the Kilogram redefinition in 2019).
History of the highest RMs for $\delta^{13}$C: carbonates, CO$_2$ extraction by reaction with H$_3$PO$_4$

1953: Belebmite from PeDee formation, CaCO$_3$-matrix. (its homogeneity cannot be taken for granted.)

1957: NBS20, Solnhofen limestone, CaCO$_3$-matrix. Later, drifts in $\delta^{18}$O and potential contaminations were reported.

1987: NBS19, homogeneous marble of unknown origin, CaCO$_3$-matrix.

2006: LSVEC (Li$_2$CO$_3$ chemical) introduced as the second-scale anchor.


2015: large drift of LSCEV $\delta^{13}$C value was reported, later its use as $\delta^{13}$C-RM discontinued.

There were urgent needs for NBS19’ replacement and LSVEC’ replacement.
Compatibility targets for stable isotope data of greenhouse gases

<table>
<thead>
<tr>
<th>Component</th>
<th>Compatibility targets, including long-term compatibility, 1-sigma</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>± 0.1 ppm (North.Hem.)</td>
</tr>
<tr>
<td></td>
<td>± 0.05 ppm (So.Hemisph)</td>
</tr>
<tr>
<td>CH₄</td>
<td>± 2 ppb</td>
</tr>
<tr>
<td>CO</td>
<td>± 2 ppb</td>
</tr>
<tr>
<td>N₂O</td>
<td>± 0.1 ppb</td>
</tr>
<tr>
<td>SF₆</td>
<td>± 0.02 ppt</td>
</tr>
<tr>
<td>H₂</td>
<td>± 2 ppb</td>
</tr>
</tbody>
</table>

Compatibility targets are based on the intended data use. Targets for δ¹³C are very strict.

The long-term compatibility can be achieved by using reliable δ¹³C-RMs with low uncertainty.
IAEA-603, Carrara marble CaCO$_3$.

Batch production, well-characterized uncertainty, storage effects eliminated by material sealing in glass ampules. IAEA-603 addresses the ISO Guide 35 requirements for RMs and also WMO requirements for greenhouse gas observations.

$\delta^{13}$C = $+2.460 \pm 0.010$‰ ($k=1$)

$\delta^{18}$O = $-2.730 \pm 0.040$‰ ($k=1$)
2018-2020: preparing new carbonate RMs covering δ\(^{13}\)C range:

Preparing new RMs for δ\(^{13}\)C
Matrix - chemical CaCO\(_3\)
Batch production (>3000 units of each RM), storage effects eliminated by sealing in glass ampules.
Uncertainty components associated with the values of new RMs:

### Major corrections:
- Cross-contamination in the ion source

### Homogeneity tests:
- Numerous 10 mg aliquots from representative selection of ampoules.

### Characterization:
- Measurements directly linking new RMs and IAEA-603

### Long-term stability:
- Maximum $\delta^{13}C$-shift due to CO$_2$ remaining in sealed ampoules.

### Raw data treatment:
- Potential bias in $\delta^{13}C$ due to $^{17}O$-correction

### Certified values and uncertainty

#### Results of homogeneity tests and stability estimations:

<table>
<thead>
<tr>
<th>New RMs</th>
<th>$\delta^{13}C$, ‰</th>
<th>Uncertainty due to homogeneity, ‰, 1-sigma</th>
<th>Max $\delta^{13}C$-shift due to CO$_2$ in ampoules</th>
<th>$\delta^{18}O$, ‰</th>
<th>Uncertainty due to homogeneity, ‰, 1-sigma</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAEA-610</td>
<td>~ -9.1</td>
<td>0.006</td>
<td>~0.005</td>
<td>~ -18.8</td>
<td>0.040</td>
</tr>
<tr>
<td>IAEA-611</td>
<td>~ -30.8</td>
<td>0.006</td>
<td>~0.001</td>
<td>~ 4.2</td>
<td>0.043</td>
</tr>
<tr>
<td>IAEA-612</td>
<td>~ -36.7</td>
<td>0.006</td>
<td>~0.002</td>
<td>~ -12.1</td>
<td>0.058</td>
</tr>
</tbody>
</table>
Preliminary estimates of combined uncertainty (k=1) for new RMs and comparison with old RMs:

\[ \delta^{13}C, \% \]

Uncertainty in \( \delta^{13}C, \% \)

\[ ~-36.7 \quad ~-30.8 \quad ~-9.1 \quad -5.76 \quad -5.01 \quad -2.460 \quad 2.49 \]

\( \delta^{13}C, \% \)

The combined uncertainty estimated for new RMs (these are marked in red) includes the uncertainty components related to the material homogeneity, stability, mass-spectrometer’ linearity and cross-contamination.

Old RMs were not assessed for the homogeneity and stability.
Summary: strategy for $\delta^{13}$C-RMs at the IAEA:

1. Primary RM, carbonate IAEA-603

2. New carbonate RMs covering range of $\delta^{13}$C values, IAEA-610, IAEA-611, IAEA-612

   Nearly done, RM's values are under review. Expected release in 2020.

3. Re-assessment of other secondary RMs (of combustible matrix) for the value consistency.

Thank you for your attention!