Developments of RMs on the artefact-based VPDB $\delta^{13}C$ scale, aiming to address GAW-WMO requirements

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These are different ranges of the VPDB scale.

Complexities:
1. Inter-comparisons can give a snapshot of a compatibility for a year 20XY only.
2. The compatibility targets imply the long-term data compatibility. Hence, one shall demonstrate that by reliable calibrations, over years.
3. These target values are at the limits of the best modern mass-spectrometry.

Q: How to reach that?  
By reliable calibrations against reliable and stable in time reference materials (RMs) only.  
There is a need in RMs with very low uncertainty.
Why the IAEA?

- IAEA operates as custodian of primary RMs (highest realization of several stable isotope scales).
- IAEA keeps & monitors primary RMs and introduces replacements.
- Regular IAEA expert meeting on stable isotope RMs.

What about GAW-WMO?

- A lot of air-CO2 isotope measurements, over may years,
- Since 2006, GAW Central Calibration Lab (CCL) for CO2 isotopes at MPI-Jena (DE), making “community scale-realization” in form of CO2-air mixtures (JRAS) traceable to primary RM from IAEA;
- Biannual WMO/IAEA meetings on CO2 and other greenhouse gas measurement techniques.

The situation:

- Agreement on pure CO2 is (was) shown to be worse compared to CO2-air samples;
- Agreements in inter-comparisons (CO2-air-samples) and in round robins (CO2-air cylinders) are still not satisfactory;
- Still, no independent verification of CCL mixtures;
- CH4-air-samples are mostly analyzed by converting CH4 to CO2. Agreement in inter-comparisons for (CH4-air-samples) is also not satisfactory. There is no CCL
$\delta^{13}C = \left( \frac{^{13}C/^{12}C_{\text{sample}}}{^{13}C/^{12}C_{\text{VPDB}}} - 1 \right)$

where VPDB (Vienna Pee dee Belemnite) is the reporting scale; $\delta$-values are expressed in multiples of 0.001, notation of $‰$

We talk about rather a large scale-range and how to pinpoint it.

Note: SI-traceability with requested uncertainty is still not realized, there is NO primary method to prepare mixtures of decided $\delta^{13}$C-$\delta^{18}$O. => Scale realization is based on the primary RM + reference method.
Practicalities of the scale:

1. Based on the primary RM in the form of Ca-carbonate:
   - Historical Pee Dee Belemnite (PDB): biological-geological carbonate;
   - NBS20 (Solenhofen): powdered limestone, $\delta^{18}$O-drifts reported;
   - NBS19: high-purity, homogeneous marble Ca-carbonate, exhausted;
   - IAEA-603: high-purity, homogeneous marble Ca-carbonate, in current use;

   Why carbonates: simple matrix, numerus labs, many aliquots in a single vial, better stability compared to CO$_2$.

2. Optimised preparation method:
   - CaCO$_3$ + H$_3$PO$_4$ reaction under standard conditions;

3. Based on the CO$_2$ mass-spectrometry (superior method):
   - $^{13}$C and $^{17}$O contribute to mass 45 (at 93.5 % and 6.5 % respectively),
   - $\delta^{13}$C calculated by correcting the raw data for $^{17}$O-contribution.

4. $\delta^{13}$C of CO$_2$-in-air on the VPDB-CO$_2$ scale:
   - CO$_2$ extracted from air, N$_2$O co-extracted;
   - Corrections: due to mass-spec memory, $^{17}$O-correction and N$_2$O-correction (~0.2 ‰ for $\delta^{13}$C).

5. Optical CO$_2$ spectrometry developed, still at larger uncertainty.
History of major RMs of the $\delta^{13}C$ scale and major revisions:

1953: First material

1957: Material aimed at PDB-scale realisation

1984: Replacement-RM for the scale-definition and scale-realisation

1957: Material aimed at PDB-scale realisation

1957: Material aimed at PDB-scale realisation

1984: Replacement-RM for the scale-definition and scale-realisation

2016: New primary RM IAEA-603

Revision (replacement) for LSVEC is needed

Q: What to do next? How to realize the scale-range with low U?
Traceability and hierarchy of RMs:

Scale-DEFINITION: concept + method including $^{17}$O correction

Primary RM, NBS19 (exhausted), now - **IAEA-603**
(stability to be checked against NBS19A reserved)

Scale-anchor(s) with lowest possible uncertainty,
(RMs under production at IAEA)

Secondary RMs,
For combustion applications

Uncertainty increase

Tertiary RMs
e.g. gas mixtures at CCL

Lab-working standards (daily operation)

Air samples

Note: some other RMs are under production at other RM producers.
**Additional dimension:**

In fact, carbonate RMs provide cover several scales, these are VPDB-$\delta^{13}$C scale, VPDB-$\delta^{18}$O scale and VPDB-CO$_2$ $\delta^{18}$O scale.
With lessons learned, how we apply that to IAEA-603 and new RMs?

- Careful material selection,
- Batch production, large number of fully identical units,
- Understanding & characterizing all major uncertainty components,
- Elimination of undesirable (storage) effects, evaluation of U(storage),

Note, here we discuss RMs in the simple matrixes. Ca-carbonates (most stable) and later pure CO2 – these can address the most critical U-requirements. Organic-matrix RMs are of lower U-tolerance and thus considered separately.
### IAEA-603 characterization by H3PO4-reaction under standard conditions

<table>
<thead>
<tr>
<th>Component</th>
<th>$\delta^{13}$C ‰ VPDB</th>
<th>$\frac{N_{\text{IAEA-603}}}{N_{\text{NBS19}}}$</th>
<th>$\delta^{18}$O ‰ VPDB-CO$_2$</th>
<th>$\frac{N_{\text{IAEA-603}}}{N_{\text{NBS19}}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homogeneity</td>
<td>±0.009 (1-σ)</td>
<td>$N_{\text{IAEA-603}} = 195$</td>
<td>±0.035 (1-σ)</td>
<td>$N_{\text{IAEA-603}} = 148$</td>
</tr>
<tr>
<td>(analytical scatter 1-σ, at &gt;95%-CI on 52000 ampoules produced)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Characterization</td>
<td>2.460±0.005</td>
<td>$N_{\text{IAEA-603}} = 38$</td>
<td>-2.373±0.017</td>
<td>$N_{\text{IAEA-603}} = 38$</td>
</tr>
<tr>
<td>(at 95%-CI)</td>
<td></td>
<td>$N_{\text{NBS19}} = 38$</td>
<td></td>
<td>$N_{\text{NBS19}} = 38$</td>
</tr>
<tr>
<td>Stability</td>
<td>Max shift of 0.003</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(potential effect due to CO$_2$ in ampoules)</td>
<td></td>
<td></td>
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<tr>
<td>Potential bias</td>
<td>~ 0.001</td>
<td></td>
<td>n/a</td>
<td></td>
</tr>
<tr>
<td>due to $^{17}$O correction</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Assigned values</td>
<td>2.460±0.010</td>
<td></td>
<td>-2.373±0.039</td>
<td></td>
</tr>
</tbody>
</table>

1. IAEA-603 guarantees the VPDB scale-realization for decades.
2. U-estimation includes U-analytical (IAEA-lab).
3. Each ampoule, each aliquot shall stay within the assigned uncertainty over years.
4. We are at the limits of the best carbonate-reparation method and the factory certificate for MAT253’ reproducibility in $\delta^{13}$C.

Note, by multiple runs one can reduce the certified uncertainty as related to the material-inhomogeneity.
IAEA-603 uncertainty contribution (in a squared form)

- Homogeneity (1-σ), including U-method: 70%
- Characterization (95% CI): 21%
- Stability (max shift): 8%
- 
- H correction (1-σ): 1%
<table>
<thead>
<tr>
<th>Category</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary RM for scale-realization</td>
<td>carbonate IAEA-603</td>
</tr>
<tr>
<td>Scale-anchors RMds</td>
<td>3 new carbonate RMds <em>(under development)</em></td>
</tr>
<tr>
<td>Scale-transfer mixtures</td>
<td>CO2-in-air</td>
</tr>
<tr>
<td></td>
<td>e.g. by GAW-CCL</td>
</tr>
<tr>
<td>Working lab-standard mixtures</td>
<td>CO2-in-air</td>
</tr>
<tr>
<td>Air-samples</td>
<td></td>
</tr>
</tbody>
</table>
Current status:

IAEA-603 is the primary RM, with a reliably estimated uncertainty, in a large quantity.

3 new carbonate RMs are under development at IAEA.
Q-1: How to realize the scale by several RMs, namely cover $\delta^{13}\text{C}-\delta^{18}\text{O}$ space, based on (traceable to) the primary RM? A: based on reference method, namely well-tested mass-spectrometry + well-understood corrections.

Q-2: How to make the traceability chain (by means of relative measurements only) without essential increase in uncertainty? A: homogeneous materials, optimized measurement procedure(s), taking multiple aliquots of solid-RMs.
\( \delta^{13}C \) and \( \delta^{18}O \) values of new carbonate RMs (under characterization):

- Verification of values for new IAEA RMs by expert labs, including runs against remaining NIST RMs 8562-8564.
- RMs will cover \( \delta^{13}C-\delta^{18}O \) space, providing means to cross-check values & verify a drift if any.
Batch preparation of new carbonate-RMs:

<table>
<thead>
<tr>
<th>RMs</th>
<th>Production, 1st batch</th>
<th>0.5 g ampoules</th>
<th>Reserved amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAEA-603</td>
<td>5200</td>
<td>1ml ampoules</td>
<td>4 batches</td>
</tr>
<tr>
<td></td>
<td>(available)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>New carbonates:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IAEA-611</td>
<td>~3750</td>
<td>2ml ampoules</td>
<td>2 batches</td>
</tr>
<tr>
<td>IAEA-610</td>
<td>~3000</td>
<td>2ml ampoules</td>
<td>3 batches</td>
</tr>
<tr>
<td>IAEA-612</td>
<td>~4100</td>
<td>2ml ampoules</td>
<td>1 batch (+2 batches similar)</td>
</tr>
<tr>
<td>NBS19A</td>
<td>~1100</td>
<td>1 ml ampoules</td>
<td>2 batches</td>
</tr>
</tbody>
</table>

IAEA-603 and new IAEA-610, -611 and -612
## Homogeneity (analytical data-scatter) and potential storage effects:

<table>
<thead>
<tr>
<th></th>
<th>$\delta^{13}C$, ‰</th>
<th>U-homogeneity at 1-σ, ‰</th>
<th>Max $\delta^{13}C$-shift due to CO$_2$ in ampoule</th>
<th>$\delta^{18}O$, ‰</th>
<th>U-homogeneity at 1-σ, ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAEA-603</td>
<td>+2.46</td>
<td>±0.009</td>
<td></td>
<td>-2.37</td>
<td>±0.035</td>
</tr>
<tr>
<td></td>
<td></td>
<td>n=198, &gt;95% CI</td>
<td></td>
<td></td>
<td>n=145, &gt;95% CI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>~0.003</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>New carbonates</th>
<th>$\delta^{13}C$, ‰</th>
<th>U (homogeneity)</th>
<th>Max $\delta^{13}C$-shift due to CO2 in ampoules</th>
<th>$\delta^{18}O$, ‰</th>
<th>U (homogeneity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAEA-611</td>
<td>~ -30.8</td>
<td>±0.008</td>
<td></td>
<td>~0.001</td>
<td>±0.042</td>
</tr>
<tr>
<td></td>
<td></td>
<td>n=78, at 67 % CI</td>
<td></td>
<td></td>
<td>n=78, at 67 % CI</td>
</tr>
<tr>
<td></td>
<td></td>
<td>~0.001</td>
<td></td>
<td>~ -3.8</td>
<td></td>
</tr>
<tr>
<td>IAEA-610</td>
<td>~ -9.1</td>
<td></td>
<td></td>
<td></td>
<td>~0.003</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>~ -18.4</td>
</tr>
<tr>
<td>IAEA-612</td>
<td>~ -36.8</td>
<td></td>
<td></td>
<td></td>
<td>~0.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>~ -11.8</td>
</tr>
</tbody>
</table>

CO$_2$ potentially available for reaction during storage:
- up to ~0.01 cm$^3$ STP CO$_2$ in sealed glass ampoules;
- ~1.2 cm$^3$ STP CO$_2$ reacted with LSVEC in vials (during long storage).

$\Rightarrow$ Ampoule-sealing is really advantageous option.
Next, works on pure CO$_2$ gas RMs
Work for CCQM Key Comparison Pilot Study on CO₂ isotopes:

Test: aliquots from BIPM-vessel (~2 bar) taken in glass transfer-vessels (the same as used for CO₂ from carbonate RMs), then connected to MAT253’ automated manifold.

\[ \delta^{13}C = -3.508 \pm 0.006 \text{‰ (1StDev, n=10 refills)} \]

\[ \delta^{18}O = -14.560 \pm 0.029 \text{‰ (1StDev, n=10 refills)} \]

MAT253 specs: 1StDev ≤ 0.010 ‰ without sample-refill

Planned verification - with carbonate RMs and NIST CO₂ RM 8562-8564
Summary:

- IAEA maintains the primary RM on the VPDB scale and introduces replacements. Well-characterized primary RM IAEA-603 was introduced in 2016 (the highest scale-realisation). IAEA-603 is homogeneous, well preserved in sealed glass ampoules, its large amount is sufficient for decades.

- IAEA works on sustainable realization of the VPDB-scale. 3 new scale-anchors (carbonate RMs) aimed at reliable scale-realisation with lowest possible uncertainty are under development, pure CO$_2$ RMs will follow.

- Scale-verification over years is foreseen, for this purpose NBS19A is reserved;

- IAEA proposes to highlight revisions of the scale-realization by names, e.g. VPDB2020.

- More metrological understanding of the VPDB scale is needed = the role of Key Comparison Pilot Study for CO$_2$ isotopes.

Knowledge dissemination:

- IAEA proposes 4-years Technical Cooperation (TC) interregional project (2020-2023) for “Capacity development towards wider use of stable isotopic techniques for source attribution of greenhouse gases in the atmosphere”.

BG1.5

Quality control tools in stable isotope measurements: Making your data reliable

Co-organized as AS5.27

Convener: Sergey Assonov | Co-conveners: Philip Dunn, Grzegorz Skrzypek, David Soto