Challenges in maintaining the artefact-based carbon stable isotope scale.

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Relative, artefact-based VPDB $\delta^{13}$C scale
(Vienna PeDe Belemnite scale, based on isotope ratios):

$$\delta^{13}C = \left( \frac{[^{13}C/^{12}C]_{\text{Sample}}}{[^{13}C/^{12}C]_{\text{VPDB}}} - 1 \right) \times 1000 \ \text{‰}$$

The IAEA - custodian of primary RMs:
- Primary standards (artefacts) are used to establish the entire calibration scheme for stable isotope ratios as delta-values, similar to former prototypes of kilogram and meter.
- Example: VPDB scale for $\delta^{13}$C and $\delta^{18}$O, with isotope ratios fixed to the (hypothetical) VPDB-artefact.
- Realization: The primary RMs distributed by the IAEA to end-users, with their lowest possible uncertainty.
- Other RMs (secondary) characterised directly against primary RMs.

Crucial requirements for $\delta^{13}$C-RMs:
- Need for long-term stability (decade-long monitoring programs),
- Low uncertainty data demanded by atmosphere monitoring community.

Low uncertainty of data $\Rightarrow$ low uncertainty RMs required

Example of CO$_2$ & $\delta^{13}$C(CO$_2$) in background air, data by NOAA/INSTAR:
- Marine air (Vienna, 1984
- South Pole (USGS, 1988) metro.
- St.Error $\Delta C = 0.02$)

Valance of $\delta^{13}$C on VPDB scale:
- $C_{\text{VPDB}}$ = 0.00‰
- Drift of RMs (if any) is easier to be detected by
- Low uncertainty data of atmospheric CO$_2$.

What is next: (i) need for introducing replacement material(s) for 2-point data normalization,
(ii) developing new RMs optimized in terms of their uncertainty;
(iii) potential revision of the VPDB scale realization.

History of the VPDB $\delta^{13}$C scale:
1957: Only one RM defining the scale
Most of natural $\delta^{13}$C values range from -50 to +5 %

1984: Replacement for PDB

2006: Second scale-anchor RM

IAEA-603: Replacement for NBS19
- Carbonate material crushed, sieved, washed. Produced $\approx 2$ kg in total.
- 5 batches of 0.2 kg.
- Each batch - IAEA ampoules (0.1g) sealed under argon. Other batches sealed for storage.
- Homogeneity study on 10 ampoules out of IAEA (at 99% confidence level).
- Characterization of the IAEA, against remaining NBS19.
- Data supported by 3 expert labs.

Uncertainty of IAEA-603 describes how well a single aliquot represents the value assigned.

Hierarchy of RMs and measurement results:

Proposed realisation with several anchors:
Realization model being similar to the temperature scale realization ITS-90. It includes definition, primary RM + several well-characterized scale-anchors of high quality:
- Definition-level: NBS19 (historical artefact, defining the VPDB scale)
- Realization:
  - IAEA-603, primary RM distributed to end-users (and NBS18A reserved to verify any drift),
  - scale-anchors: three new carbonate RMs under characterization at the IAEA,
  - NIST CO$_2$ RMs (nearly exhausted), to be used to verify consistency of new RMs,
  - new CO$_2$ RMs (planned at the IAEA),
Note: other RMs can be developed (e.g. USGS44 being under development at USGS).

Advantages:
- One can select RMs (carbonates or CO$_2$) and $\delta^{13}$C/$\delta^{18}$O values suitable for applications,
- The $\delta^{18}$O correlation applied to users of the raw data can be verified,
- Drift of RMs (if any) is easier to be detected by cross-measurements among.