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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 copes (before the Kilogram redefinition in 2019).

History of the highest RMs for $\delta^{13}C$:

carbonates, CO_2 extraction by reaction with H_3PO_4

From: https://en.wikipedia.org/wiki/Belemnitida

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_2CO_3 chemical) introduced as the second-scale anchor.

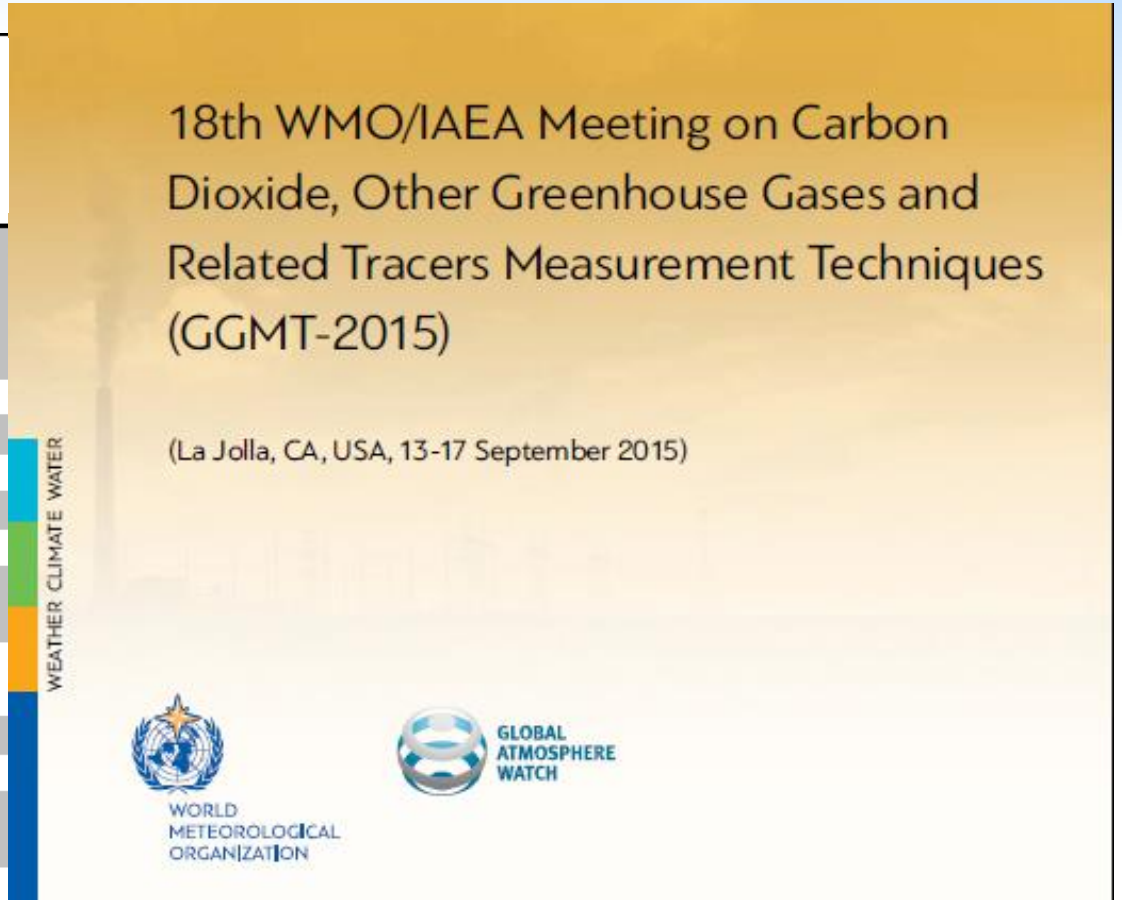
2009: NBS19 exhausted. Preparation of its replacement started.

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.

Why we need low uncertainty for high-level RMs:
Compatibility targets for stable isotope data of greenhouse gases

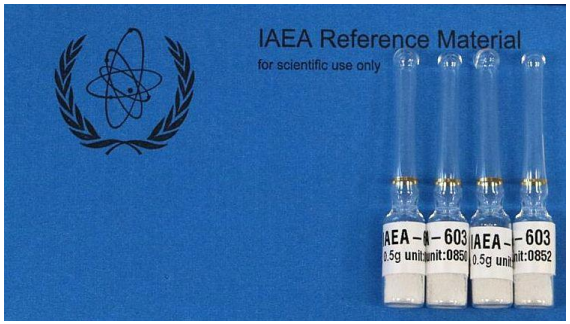
Component	Compatibility targets, including long-term compatibility, 1-sigma
CO_2	± 0.1 ppm (North.Hem.) ± 0.05 ppm (So.Hemisph)
CH_4	± 2 ppb
CO	± 2 ppb
N_2O	± 0.1 ppb
SF_6	± 0.02 ppt
H_2	± 2 ppb
$\delta^{13}C\text{-}CO_2$	± 0.01‰
$\delta\,^{18}O\text{-}CO_2$	± 0.05‰
$\delta\,^{13}C\text{-}CH_4$	± 0.02‰
$\delta\,D\text{-}CH_4$	± 1‰



Compatibility targets are based on the intended data use. Targets for $\delta^{13}C$ are very strict.

The long-term compatibility can be achieved by using reliable $\delta^{13}C$-RMs with low uncertainty.

2016: release of IAEA-603, replacement for NBS19 ✓ Done



IAEA-603, Carrara marble $CaCO_3$.

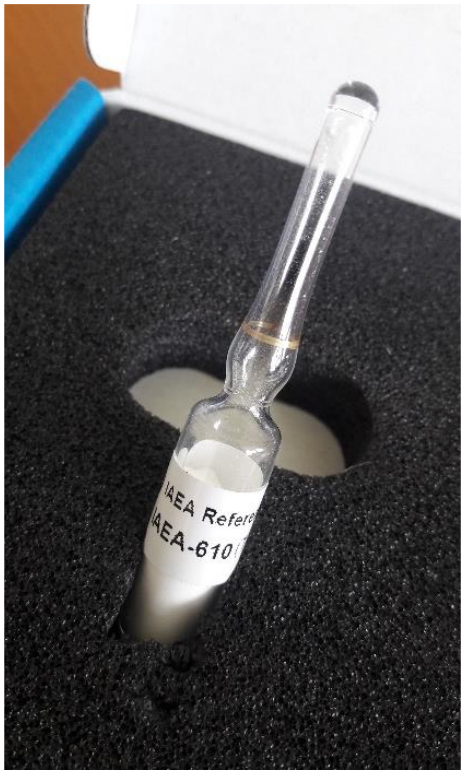
Batch production, well-characterized uncertainty, storage effects eliminated by material sealing in glass ampules.
IAEA-603 addresses the ISO Guide 35 requirements for RMs and also WMO requirements for greenhouse gas observations.

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

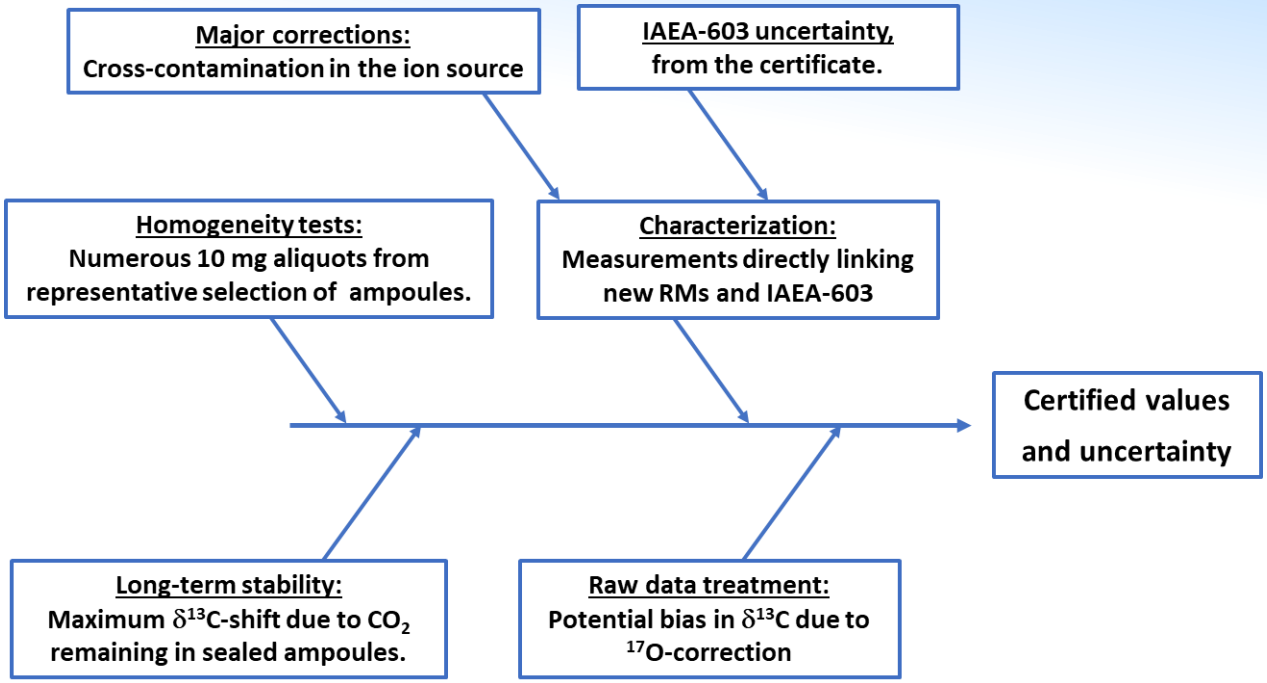
$\delta^{18}O$= -2.730 ± 0.040 ‰ (k=1)

2018-2020: preparing new carbonate RMs covering $\delta^{13}C$ range:

Preparing new RMs for $\delta^{13}C$
Matrix - chemical $CaCO_3$
Batch production (>3000 units of each RM), storage effects eliminated by sealing in glass ampules.



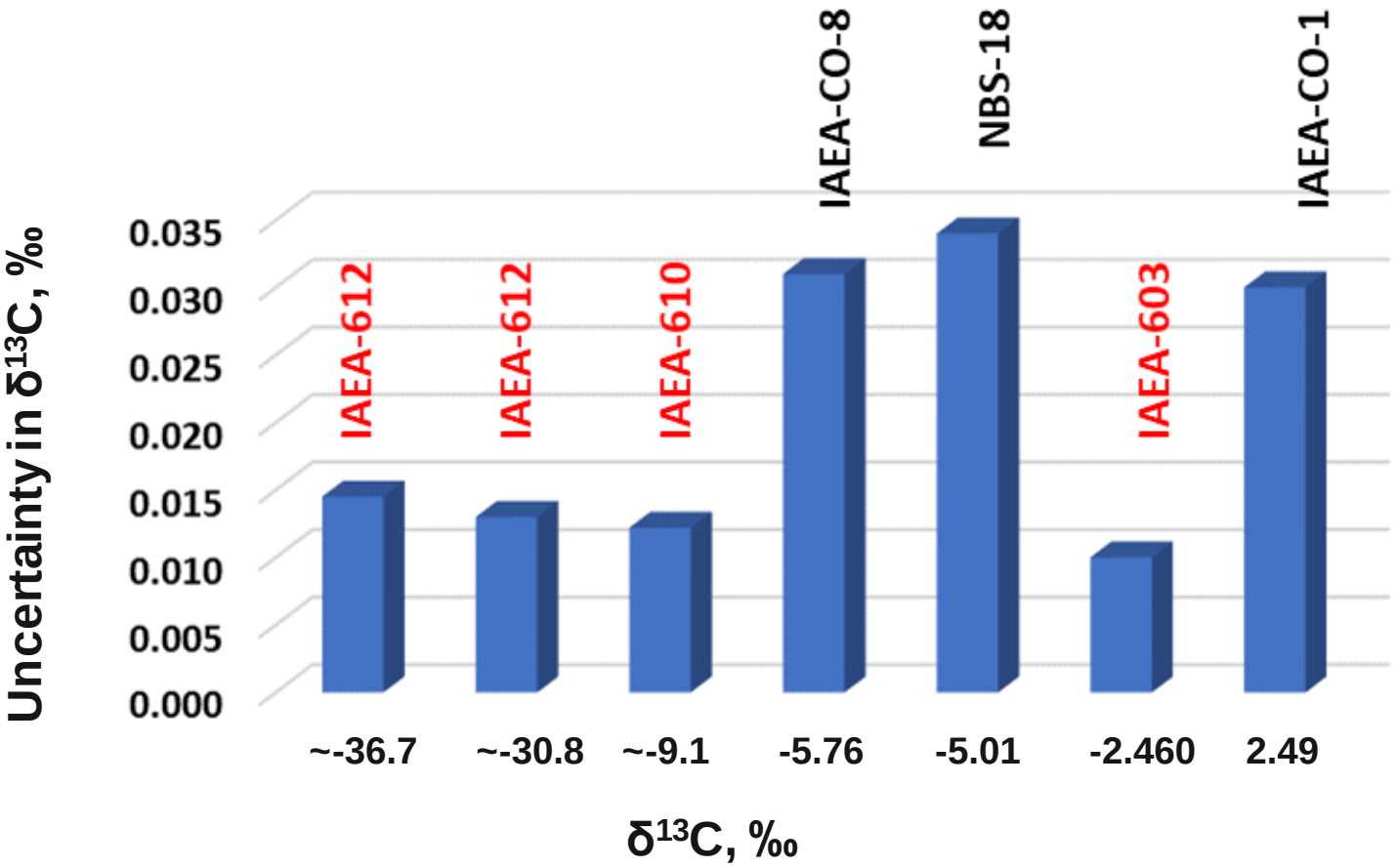
Uncertainty components associated with the values of new RMs:



Results of homogeneity tests and stability estimations:

New RMs	$\delta^{13}C$, ‰	Uncertainty due to homogeneity, ‰, 1-sigma	Max $\delta^{13}C$-shift due to CO_2 in ampoules	$\delta^{18}O$, ‰	Uncertainty due to homogeneity, ‰, 1-sigma
IAEA-610	~ -9.1	0.006	~0.005	~ -18.8	0.040
IAEA-611	~ -30.8	0.006	~0.001	~ 4.2	0.043
IAEA-612	~ -36.7	0.006	~0.002	~ -12.1	0.058

Preliminary estimates of combined uncertainty (k=1) for new RMs and comparison with old RMs:



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.

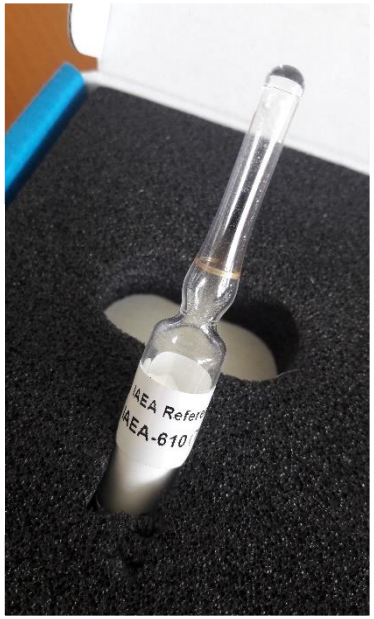
Old RMs were not assessed for the homogeneity and stability.

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!