IAEA 60 Years
Atoms for Peace and Development

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

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Table 1. Recommended network compatibility of measurements within the scope of WMO/GAW

Component	*Network compatibility goal*[1]	*Extended network compatibility goal*[2]	*Range in unpolluted troposphere (approx. range for 2017)*
$\delta^{13}C\text{-}CO_2$	0.01 ‰	0.1 ‰	-9.5 to -7.5 ‰ (VPDB)
$\delta^{13}C\text{-}CH_4$	0.02 ‰	0.2 ‰	-51 to -46 ‰ (VPDB)

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

δ-notation: the scale-unit, data reporting and scale-range

$\delta^{13}C = ({}^{13}C/{}^{12}C_{sample} \,/\, {}^{13}C/{}^{12}C_{VPDB} - 1)$

where VPDB (Vienna Pee dee Belemnite) is the reporting scale;

δ-values are expressed in multiples of 0.001, notation of ‰

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

$\delta^{13}C$= -51.000 ‰ VPDB

$\delta^{13}C$= 0.000 ‰ VPDB

$\delta^{13}C$= 2.460 ‰ VPDB

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.

Carrara marble

2. Optimised preparation method:
   - $CaCO_3 + H_3PO_4$ 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.

Depending on the algorithm, $\delta^{13}C$-value calculated for the same LSVEC-raw data differs for 0.13 ‰.

Verkouteren, 2004

4. $\delta^{13}C$ of CO_2-in-air on the VPDB-CO_2 scale:
   - CO_2 extracted from air, N_2O co-extracted;
   - Corrections: due to mass-spec memory, ^{17}O-correction and N_2O-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

PDB $\delta^{13}C$

$\delta^{13}C$= 0 ‰

1957: Material aimed at PDB-scale realisation

NBS20

$\delta^{13}C$= -1.06 ‰

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

NBS19 (**V-PDB** scale)

A few more RMs

$\delta^{13}C$= 1.95 ±0.00 ‰
(scale-definition + realisation)

2006: LSVEC, 2nd anchor on the VPDB scale

NBS19

$\delta^{13}C$= -46.60 ±0.00 ‰
(scale-normalization)

Other RMs – values modified

$\delta^{13}C$= 1.95 ±0.00 ‰
(scale-definition + realisation)

2015: LSVEC-drift found

$\delta^{13}C$= -46.60 ±0.15 ‰
(withdrawn from use)

Other RMs – values to be verified?

2016: new primary RM IAEA-603

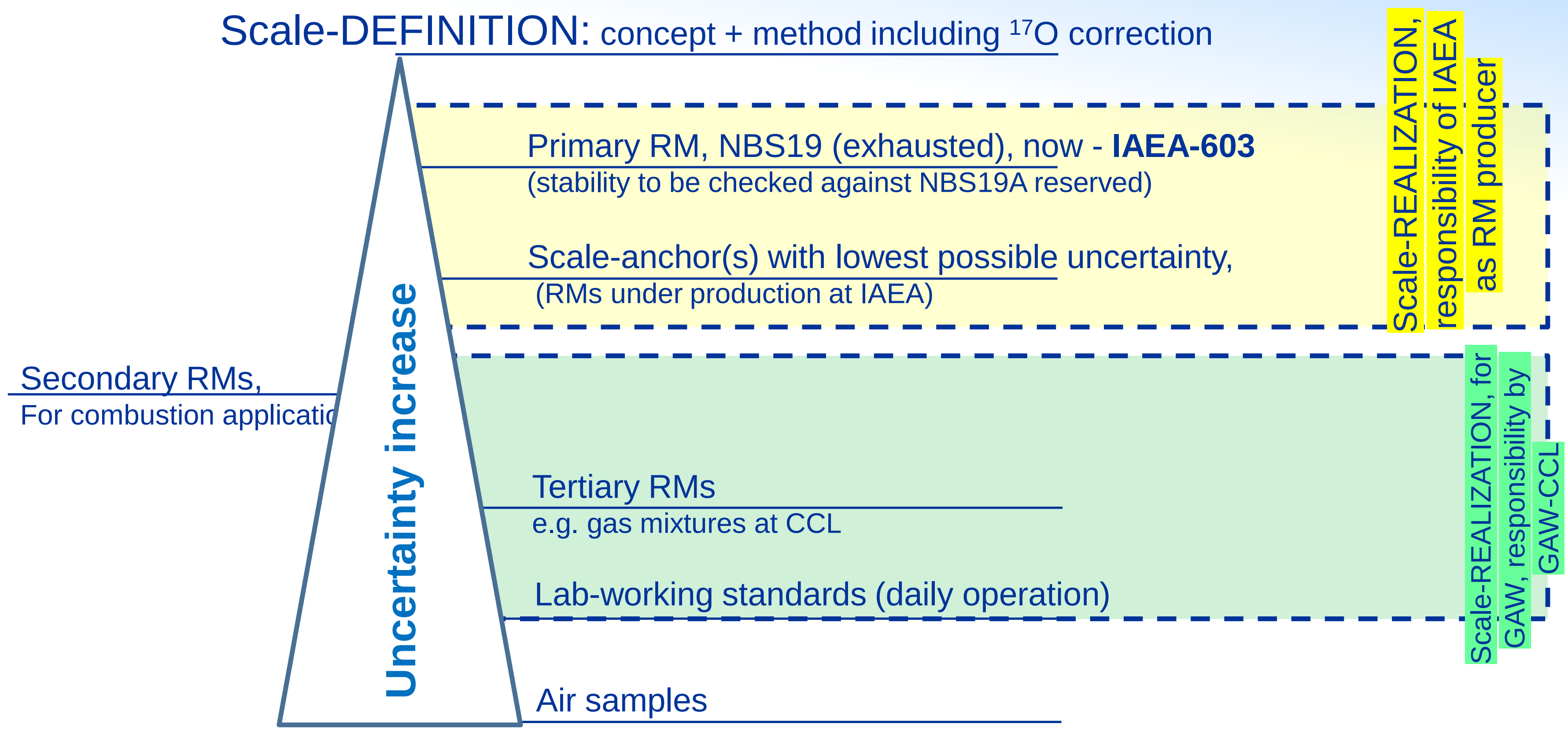
Revision (replacement) for LSVEC is needed

IAEA-603

$\delta^{13}C$= 2.46 **±0.010 ‰**
(scale-realisation)

Q: What to do next? How to realize the scale-range with low U?

Traceability and hierarchy of RMs:



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-CO2 $\delta^{18}O$ 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),

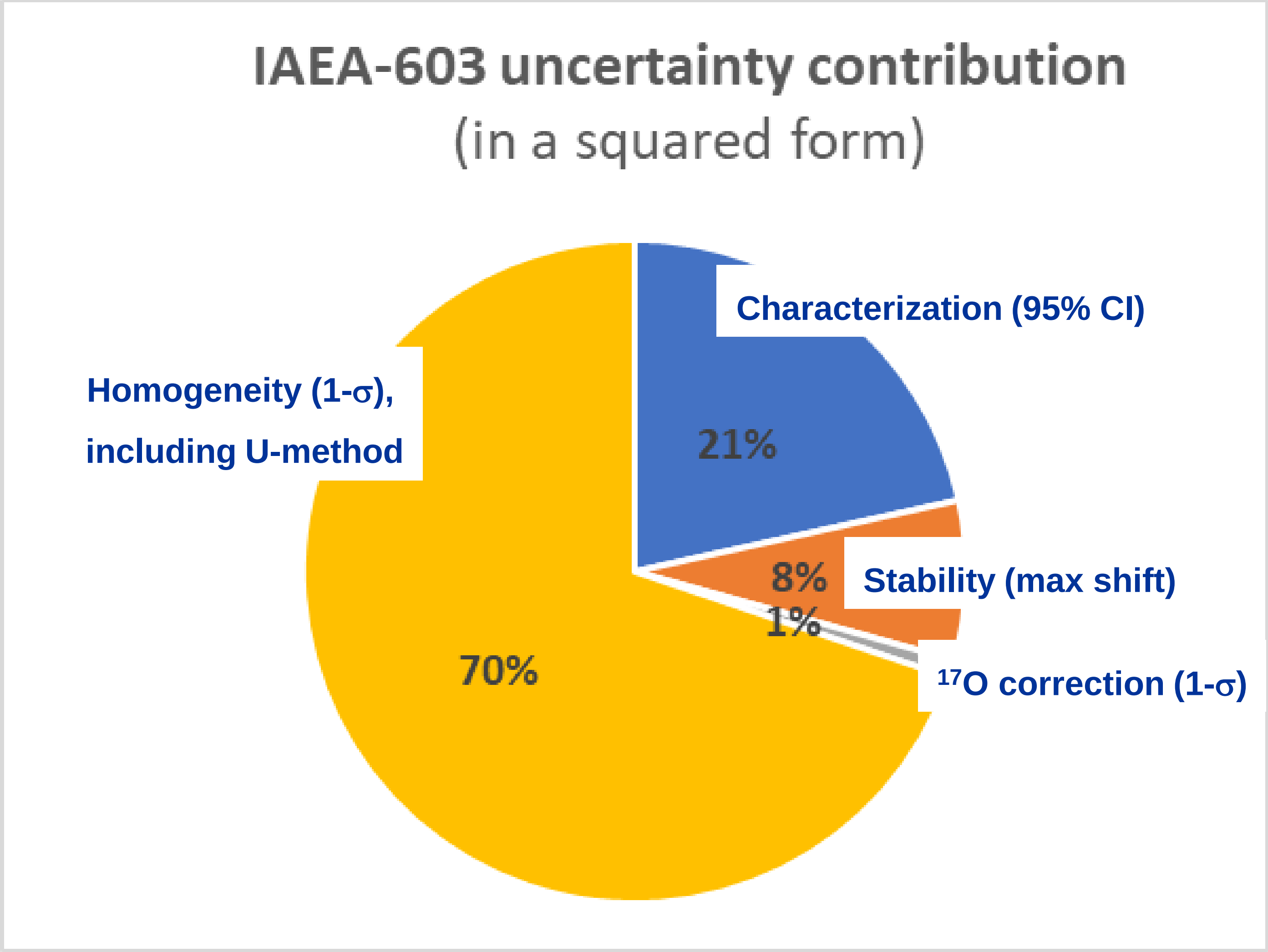
Note, here we discuss RMs in the simple matrixes. Ca-carbonates (most stable) and later pure CO2 – these can address the most critical U-requirements. Organic-matrix RMs are of lower U-tolerance and thus considered separately.

IAEA-603 characterization by H3PO4-reaction under standard conditions

Component	$\delta^{13}C$ ‰ VPDB	$N_{IAEA-603}$ / N_{NBS19}	$\delta^{18}O$ ‰ VPDB-CO_2	$N_{IAEA-603}$ / N_{NBS19}
Homogeneity (analytical scatter 1-σ, at >95%-CI on 52000 ampoules produced)	±0.009 (1-σ)	$N_{IAEA-603}$ = 195	±0.035 (1-σ)	$N_{IAEA-603}$ = 148
Characterization (at 95%-CI)	2.460±0.005	$N_{IAEA-603}$ =38 N_{NBS19}=38	-2.373±0.017	$N_{IAEA-603}$ =38 N_{NBS19}=38
Stability (potential effect due to CO_2 in ampoules)	Max shift of 0.003			
Potential bias due to ^{17}O correction	~ 0.001		n/a	
Assigned values	**2.460±0.010**		**-2.373±0.039**	

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)
Characterization (95% CI)
21%
Homogeneity (1-σ),
including U-method
70%
8%
Stability (max shift)
1%
17O correction (1-σ)

Traceability and <u>commutability</u> of RMs (closeness of properties)

Primary RM for scale-realization	**carbonate IAEA-603**
Scale-anchors RMs	3 new carbonate RMs (*under development)*
	Pure CO2 RMs will be developed later, at IAEA
Scale-transfer mixtures	CO2-in-air e.g. by GAW-CCL
Working lab-standard mixtures	CO2-in-air
Air-samples	

Uncertainty

Current status:

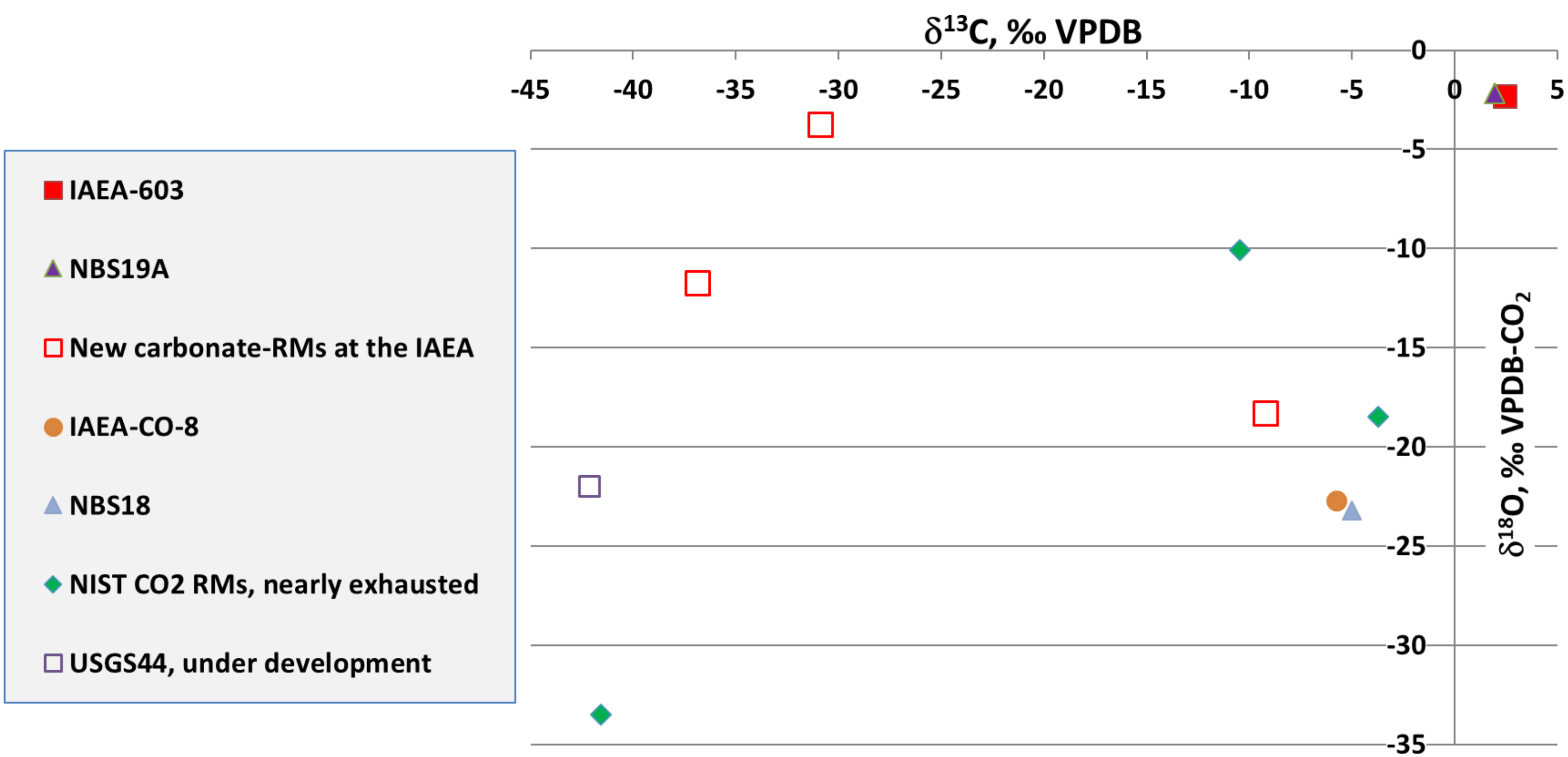
IAEA-603 is the primary RM, with a reliably estimated uncertainty, in a large quantity.

3 new carbonate RMs are under development at IAEA.

Q-1: How to realize the scale by several RMs, namely cover $\delta^{13}C$-$\delta^{18}O$ space, based on (traceable to) the primary RM?
A: based on refence 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):

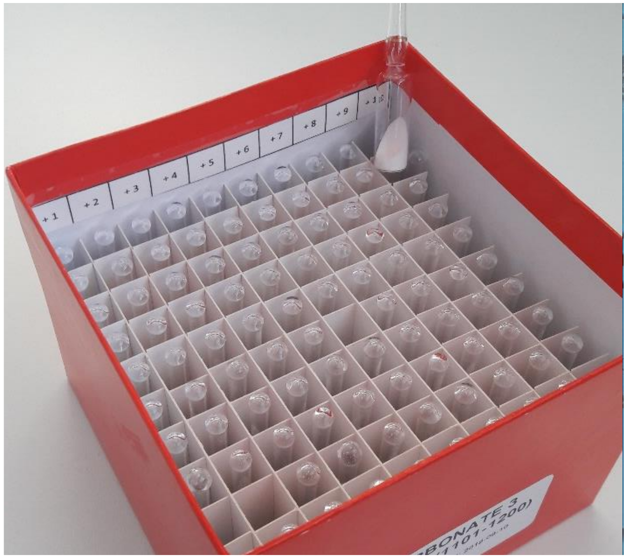
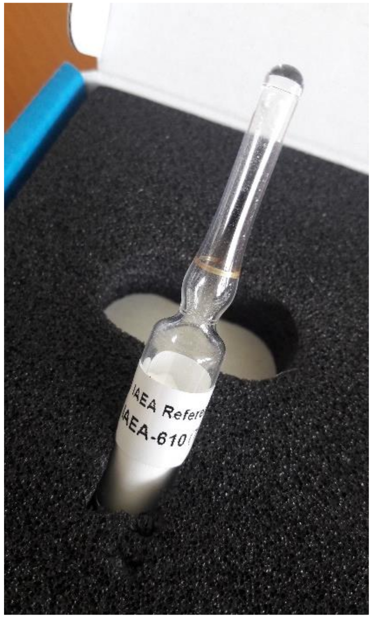
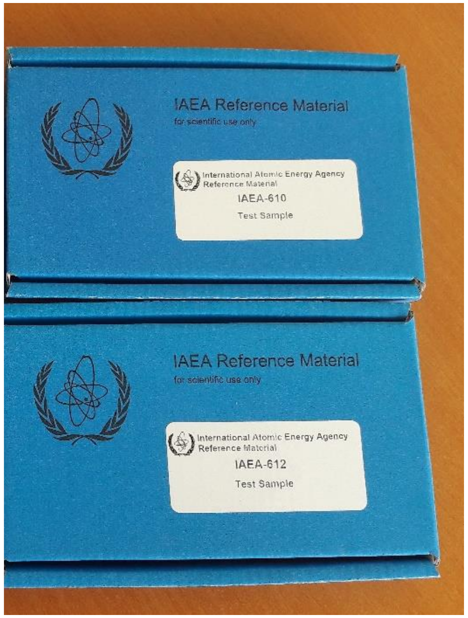


- Verification of values for new IAEA RMs by expert labs, including runs against remaining NIST RMs 8562-8564.
- RMs will cover $\delta^{13}C$-$\delta^{18}O$ space, providing means to cross-check values & verify a drift if any.

Batch preparation of new carbonate-RMs:

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

IAEA-603 and new IAEA-610, -611 and -612

Homogeneity (analytical data-scatter) and potential storage effects:

	$\delta^{13}C$, ‰	U-homogeneity at 1-σ, ‰	Max $\delta^{13}C$-shift due to CO_2 in ampoule	$\delta^{18}O$, ‰	U-homogeneity at 1-σ, ‰
IAEA-603	+2.46	±0.009 n=198, >95% CI	~0.003	-2.37	±0.035 homogeneity n=145, >95% CI

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

CO_2 potentially available for reaction during storage:

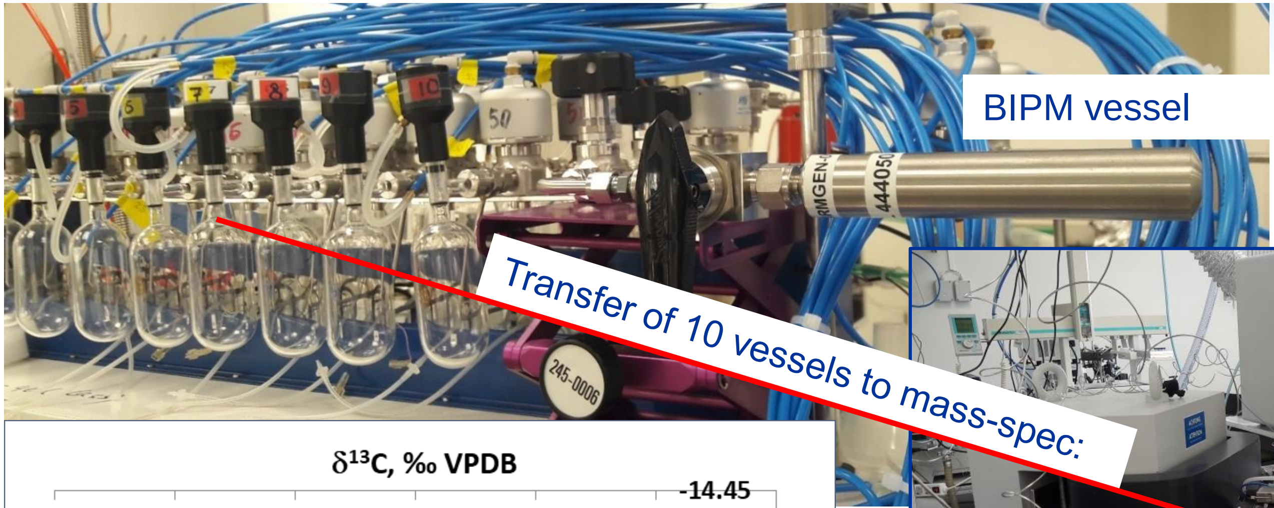
- up to ~0.01 cm^3 STP CO_2 in sealed glass ampoules;
- ~1.2 cm^3 STP CO_2 reacted with LSVEC in vials (during long storage).

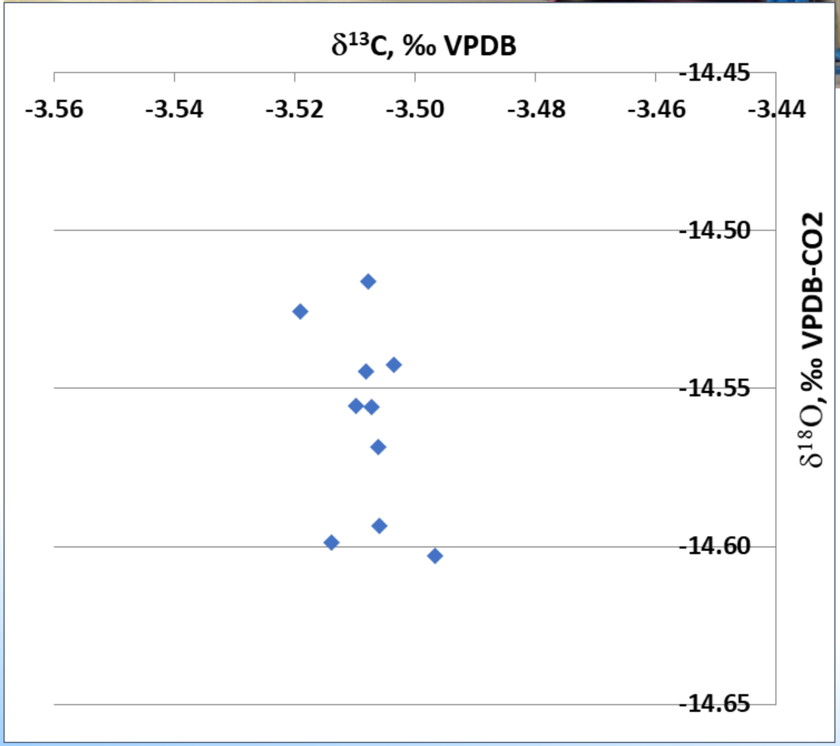
=> Ampoule-sealing is really advantageous option.

Next, works on pure CO_2 gas RMs

Work for CCQM Key Comparison Pilot Study on CO_2 isotopes:

Test: aliquots from BIPM-vessel (~2 bar) taken in glass transfer-vessels (the same as used for CO_2 from carbonate RMs), then connected to MAT253' automated manifold.





$\delta^{13}C$= -3.508 ± 0.006 ‰ (1StDev, n=10 refills)

$\delta^{18}O$= -14.560 ± 0.029 ‰ (1StDev, n=10 refills)

Planned verification - with carbonate RMs and NIST CO_2 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".