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

S. Assonov, M. Gröning and A. Fajgelj, International Atomic Energy Agency (IAEA)

IAEA
International Atomic Energy Agency

P7
CCQM Workshop on "Advances in Metrology in Chemistry and Biology", 9-10 April, 2019

Relative, artefact-based VPDB δ^{13}C scale

(Vienna PeDee Belemnite scale, based on isotope ratios):

$$\delta^{13}C = [(^{13}C/^{12}C)_{Sample}/(^{13}C/^{12}C)_{VPDB} - 1]$$

The IAEA - custodian of primary RMs:

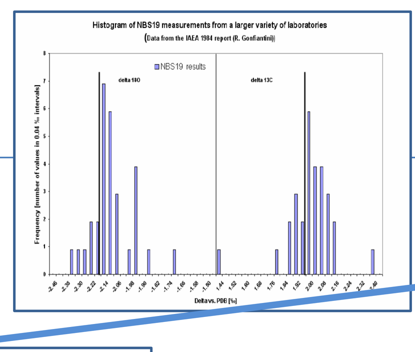
- Primary standards (artefacts) are used to establish the entire calibration scheme for stable isotope ratios as delta-values, similar to former prototypes of *kilogram* and *meter*. Example: VPDB scale for δ^{13}C and δ^{18}O, with isotope ratios fixed to the (hypothetical) VPDB-artefact.
- Realization: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

History of the VPDB δ^{13}C scale:

1957: Only one RM defining the scale

PDB
δ^{13}C= 0 ‰ (scale-definition)

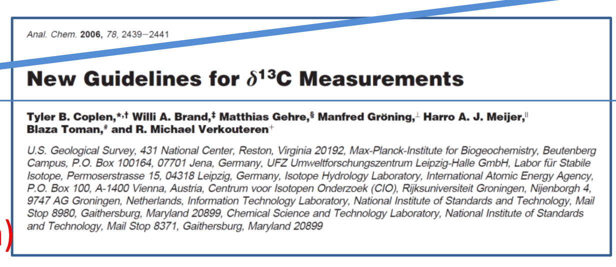
Most of natural δ^{13}C values range from -50 to +5 ‰



1984: Replacement for PDB

NBS19
δ^{13}C= 1.95 ‰±0.00 vs. PDB
scale-definition for VPDB

2006: Second scale-anchor RM



LSVEC
δ^{13}C= -46.60 ‰ ±0.00
(defines the scale span, RM for data normalisation)

NBS19
δ^{13}C= 1.95 ‰±0.00

2011- 2016: Work on the replacement of NBS19

IAEA-603

2015: LSVEC-problem, drift is found for δ^{13}C of LSVEC (data scatter ~0.35 ‰)

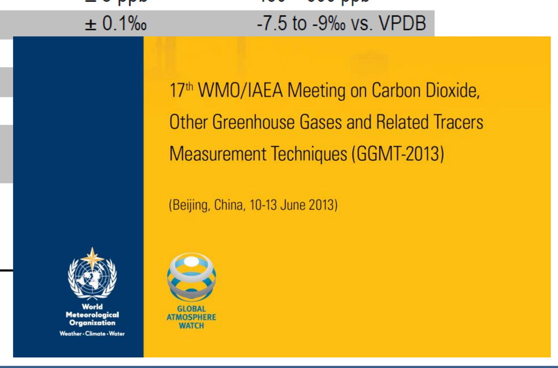
Crucial requirements for δ^{13}C-RMs:

- Need for long-term stability (decade-long monitoring programs),
- Low uncertainty data demanded by atmosphere monitoring community.

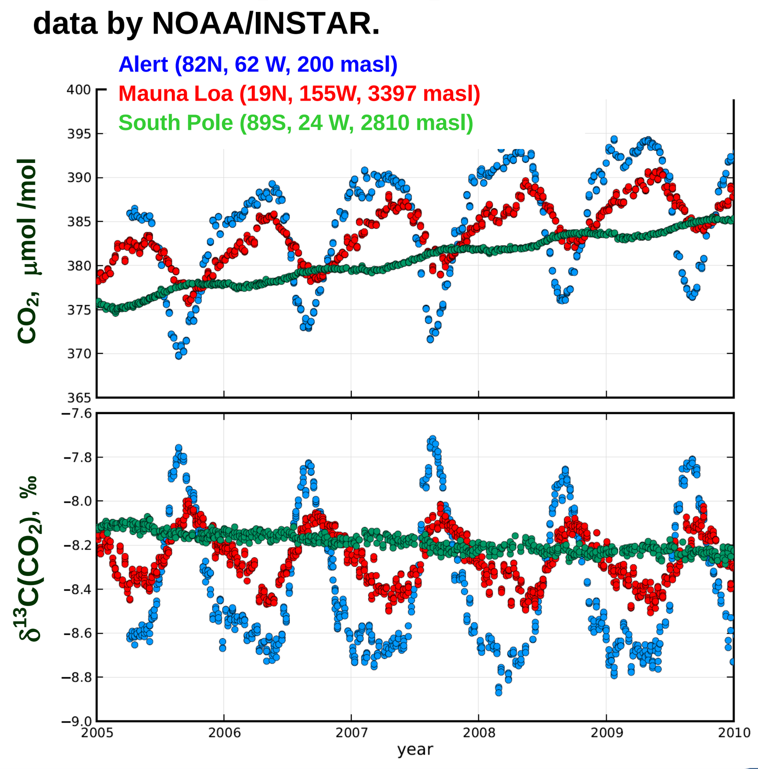
Low uncertainty of data => low uncertainty RMs required

Table 1- Recommended compatibility of measurements within the scope of GGMT

Component	Compatibility goal	Extended compatibility goal	Range in unpolluted troposphere
CO_2	± 0.1 ppm (Northern hemisphere) ± 0.05 ppm (South. hemisphere)	± 0.2 ppm	360 - 450 ppm
CH_4	± 2 ppb	± 5 ppb	1700 – 2100 ppb
CO	± 2 ppb	± 5 ppb	30 – 300 ppb
N_2O	± 0.1 ppb	± 0.3 ppb	320 – 335 ppb
SF_6	± 0.02 ppt	± 0.05 ppt	6 – 10 ppt
H_2	± 2 ppb	± 5 ppb	450 – 600 ppb
$\delta^{13}C$-CO_2	± 0.01‰	± 0.1‰	-7.5 to -9‰ vs. VPDB
$\delta^{18}O$-CO_2	± 0.05‰		
$\Delta^{14}C$-CO_2	± 0.5‰		
$\Delta^{14}C$-CH_4	± 0.5‰		
$\Delta^{14}C$-CO	± 2 molecules cm^{-3}		
$\delta^{13}C$-CH_4	± 0.02‰		
δD-CH_4	± 1‰		
O_2/N_2	± 2 per meg		

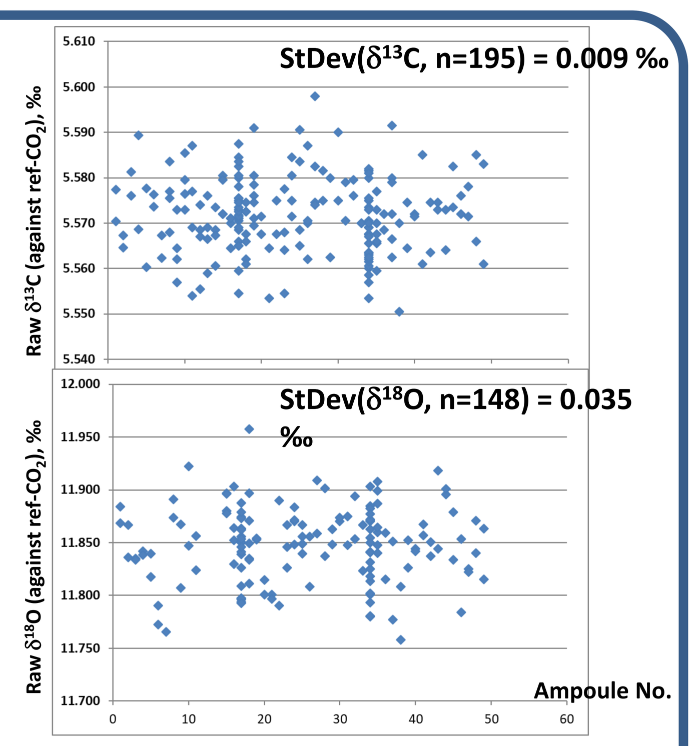


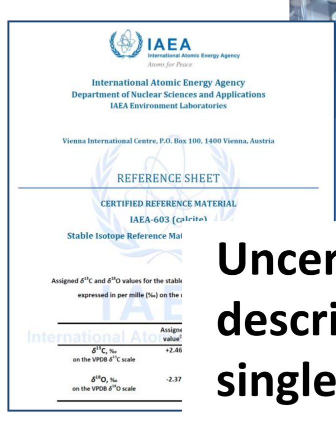
Example of CO_2 & $\delta^{13}C(CO_2)$ in background air, data by NOAA/INSTAR.



IAEA-603: Replacement for NBS19

- Carrara marble crushed, sieved, washed. Produced ~15kg in total.
- 5 batches of 2.8 kg.
- First batch - 5000 ampoules (0.5g) sealed under argon. Other batches sealed for storage.
- Homogeneity study on 52 ampoules out of 5000 (at 99.5% confidence level).
- Characterization at 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.

Characterisation:
$N_{IAEA-603}$=38, N_{NBS19}=38,
U taken as t*St.Error
U-13C=0.005 ‰
U-18O=0.017 ‰

Homogeneity study,
U taken as St.Dev.
U-13C=0.009 ‰
U-18O=0.035 ‰

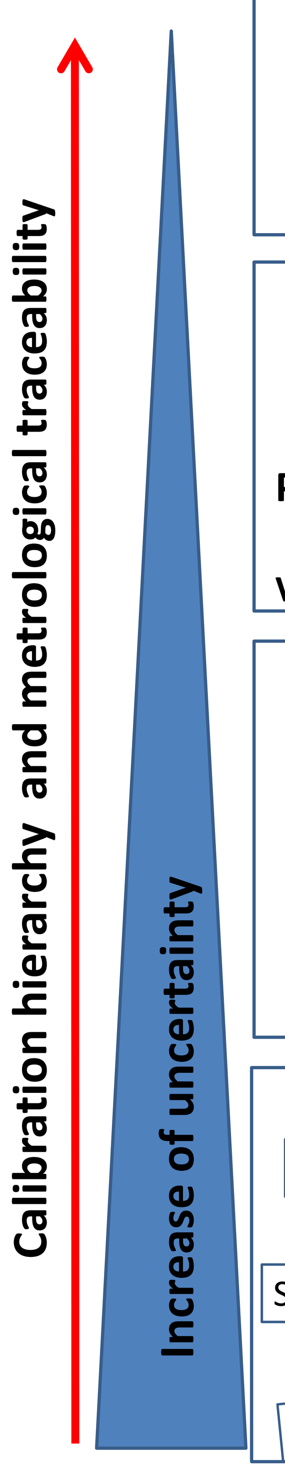
Certified values & Uncertainty
U-13C=0.01 ‰ (k=1)
U-18O=0.04 ‰ (k=1)

Long-term stability:
Not included.
Measures taken to prevent alteration.

2 point normalisation:
Not needed due to very close distance to NBS19.

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.

Hierarchy of RMs and measurement results:



Unit-definition artefacts, like VSMOW & VPDB

Calibration → IRMS at IAEA & expert labs

Measurement

Primary RMs aimed at the scale realisation, VSMOW2 & IAEA-603

Calibration → IRMS at IAEA & expert labs

Measurement

International RMs, (secondary level RMs), NBS18, NBS22, CH-7 etc

Calibration → IRMS at user laboratories

Measurement

Lab standards:
Samples, Lab A
Samples, Lab B
Samples, Lab C
Samples, Lab D
Samples, Lab E

Each additional measurement step increases the combined uncertainty.
Note, RM producers have the same instruments as end-users.
Q: how to optimise new RMs and the scale realization scheme?

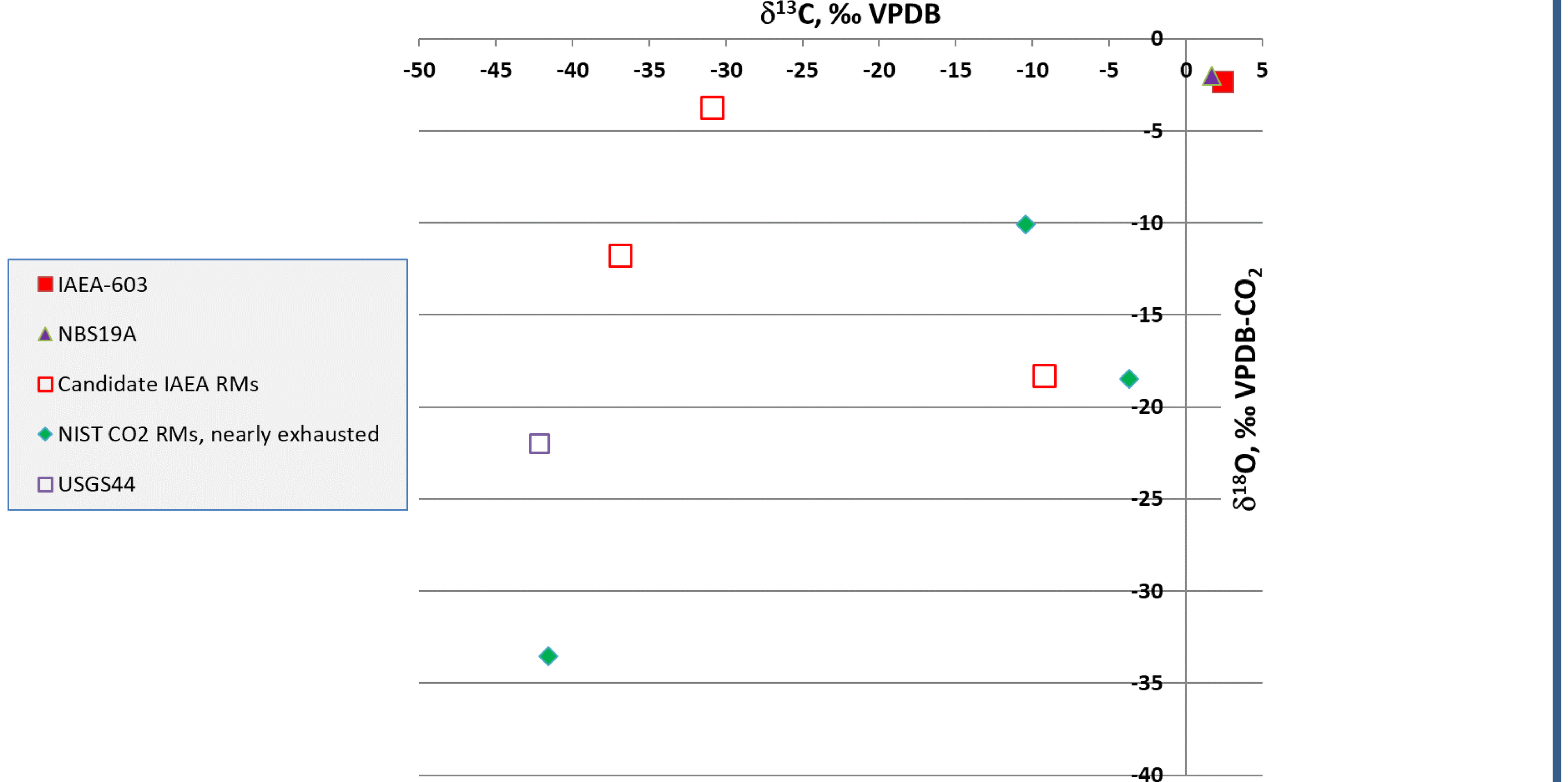
Proposed realisation with several anchors:

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 NBS19A 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 δ^{13}C-δ^{18}O values suitable for applications,**
- **The ^{17}O correction applied by users to the raw data can be verified,**
- **Drift of RMs (if any) is easier to be detected by cross-measurements among.**