UK NATIONAL MEASUREMENT LABORATORY FOR CHEMICAL AND BIO-MEASUREMENT HOSTED AT LGC

SI-traceable carbon isotope ratios

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Measurement standards for isotope delta

- International Measurement Standards
  - Adopted by convention
  - Zero-point of scale
  - Exact isotope delta
  - Can be a reference material, homogenous natural reservoir or virtual material
  - Can be more than one for each element (e.g. oxygen) but only one per scale
  - E.g. VSMOW, NIST SRM 987, NBS 28, atmospheric nitrogen, SMOB, etc.

- Primary measurement standards
  - Adopted by convention
  - Exact isotope delta (can be non-zero)
  - Can be more than one per scale
  - E.g. SLAP, IAEA-S-1, USGS32, etc.

- Primary reference materials
  - Adopted by convention
  - Exact zero or non-zero isotope delta ("replacement" materials bear uncertainty)
  - Realisations of primary and international measurement standards
  - E.g. VSMOW2, SLAP2, IRMM-014, etc.

Measurement standards for carbon isotope delta

	International Measurement Standard	Primary Measurement Standard(s)	Primary Reference Material(s)	
1950s	**PDB**	**PDB**	**PDB**	Peedee Belemnite calcium carbonate from South Carolina. $\delta^{13}C_{PDB}$ of PDB = 0 by definition.
1984	**VPDB**	**NBS 19**	**NBS 19**	PDB exhausted new scale created (numerically consistent) $\delta^{13}C_{VPDB}$ of NBS 19 = +1.95‰ exactly
2006	**VPDB**	**NBS 19** **LSVEC**	**NBS 19** **LSVEC**	Additional primary measurement standard $\delta^{13}C_{VPDB}$ of LSVEC = -46.6‰ exactly
2016	**VPDB**	**NBS 19** **LSVEC**	**(NBS 19)** **IAEA-603** **LSVEC**	NBS 19 exhausted Replaced by IAEA-603 $\delta^{13}C_{VPDB}$ of IAEA-603 = (+2.46 ± 0.02)‰

Problem with LSVEC uncovered in 2015-16

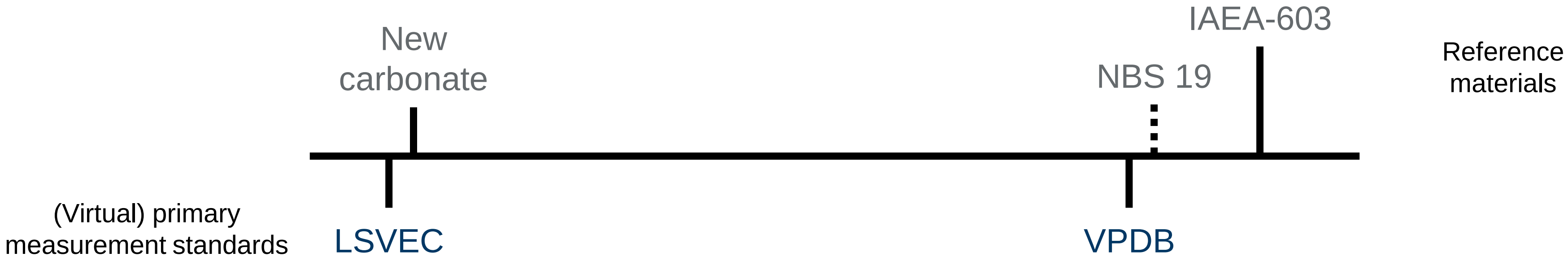
- IAEA noticed that carbon isotope ratio of LSVEC varied between different storage containers.
- Result of water present in original material (as well as that adsorbed from the atmosphere during use).
  - Atmospheric CO_2 ($\delta^{13}C_{VPDB}$ ~ -8 ‰) absorbed by water and then exchanges with carbonate.
- Withdrawn from sale (for C) – but remains within traceability chain

	International Measurement Standard	Primary Measurement Standard(s)	Primary Reference Material(s)	
2016	**VPDB**	**NBS 19** **(LSVEC)**	**(NBS 19)** **IAEA-603**	LSVEC problem uncovered – withdrawn from sale

Possible options for addressing the LSVEC problem

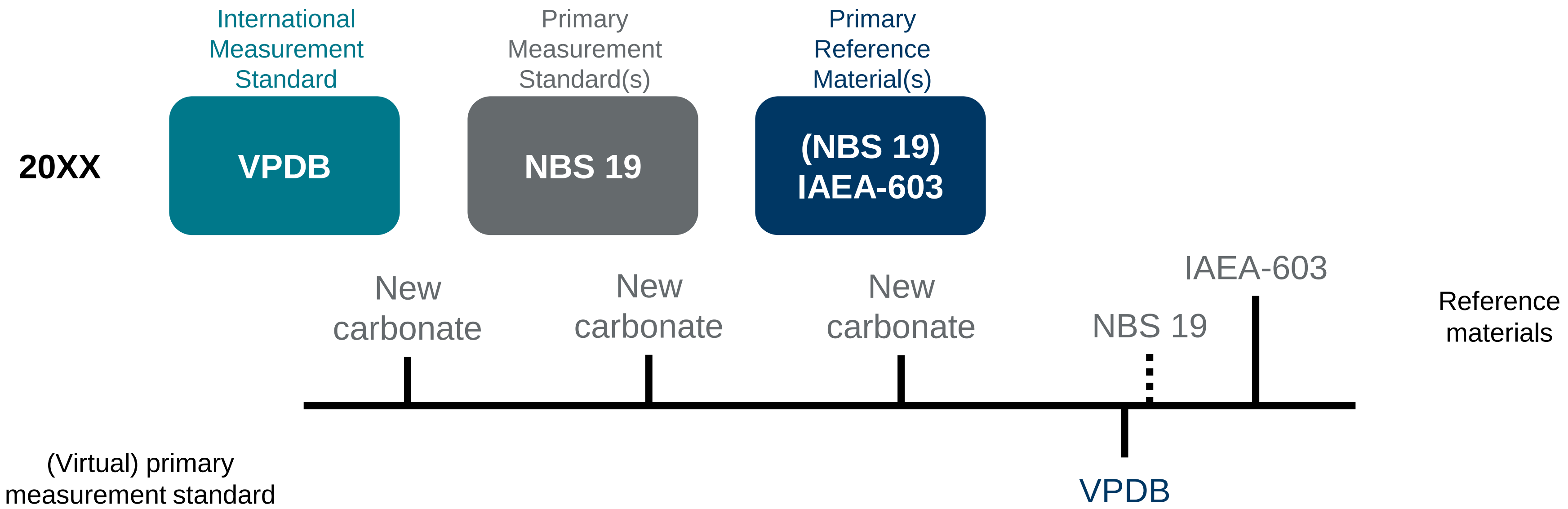
- Replace it with another carbonate and maintain the current (2006) scale
  - Effectively defines a "virtual LSVEC" at $\delta^{13}C_{VPDB}$ = -46.6 ‰
  - All other existing RMs retain their currently-assigned values.
  - LSVEC physical material still not for C isotope analysis – potentially very confusing.

	International Measurement Standard	Primary Measurement Standard(s)	Primary Reference Material(s)
20XX	**VPDB**	**NBS 19** **LSVEC**	**(NBS 19)** **IAEA-603** **New RM**



Possible options for addressing the LSVEC problem

- Replace it with other carbonate(s) and change the scale
  - New range of carbonate RMs calibrated to IAEA-603 (secondary RMs)
  - Need to re-assess all other RMs to provide assigned values on new scale.
  - Resultant need to change terminology for scales – e.g. include year.



Artefact-based scales vs the SI

- Scales traceable to an artefact
  - Can develop independently (e.g. oxygen isotope-delta scales).
  - Need to maintain the scale (drift in reference artefacts, difficult/impossible to regenerate).
  - Provide very consistent and precise results.

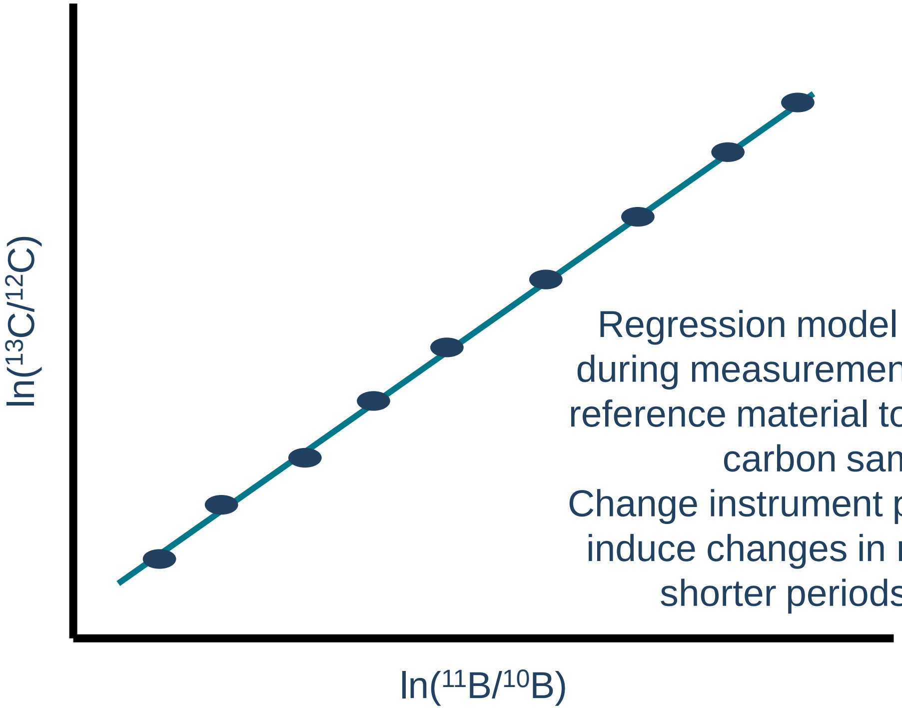
$$\delta^{13}\mathrm{C} = \frac{^{13}R_{sample}}{^{13}R_{standard}} - 1$$

- Scales traceable the SI (i.e. a measurement process).
  - Provide accurate results.
  - Can have more than one source.
  - Enhanced metrological traceability and/or comparability

$$^{13}R_{sample}$$

Alternative to relative (i.e. delta) measurements

- Mass spectrometers are precise but not accurate
- Need materials with known isotope ratio for calibration
  - Reference material(s) with known absolute isotope ratio
  - Reference material of a different element with known isotope ratio

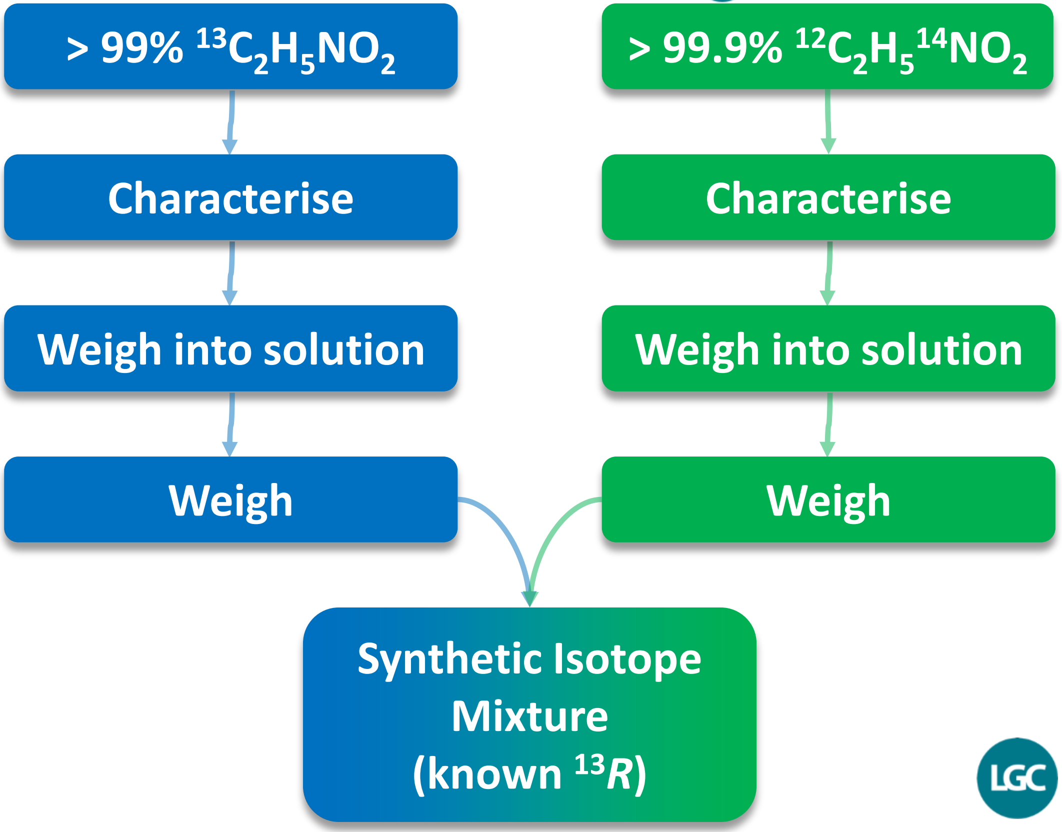


Regression model linking bias during measurements of a boron reference material to an unknown carbon sample

Change instrument parameters to induce changes in mass bias in shorter periods of time

Alternative to relative (i.e. delta) measurements

- Mass spectrometers are precise but not accurate
- Need materials with known isotope ratio for calibration
  - Reference material(s) with known absolute isotope ratio
  - Reference material of a different element with known isotope ratio
  - Gravimetric preparation of mixtures of isotopes (or isotopologues) with known purity



Absolute carbon isotope ratio measurements at LGC

2008	*Anal. Chem.* **2008**, *80*, 5963–5969 **Precise and Traceable $^{13}C/^{12}C$ Isotope Amount Ratios by Multicollector ICPMS** **Rebeca Santamaria-Fernandez,* David Carter, and Ruth Hearn** *LGC, Queens Road, Teddington, Middlesex, TW11 0LY, U.K.*	MC-ICP-MS used to determine absolute carbon isotope ratios for the first time. Mass bias corrected using NIST Boron CRM as internal standard
2013	JAAS RSCPublishing PAPER View Article Online View Journal | View Issue Cite this: *J. Anal. At. Spectrom.*, 2013, **28**, 1760 Determination of absolute $^{13}C/^{12}C$ isotope amount ratios by MC-ICPMS using calibration with synthetic isotope mixtures Dmitry Malinovsky,* Philip J. H. Dunn and Heidi Goenaga-Infante	Use of synthetic isotopologue mixtures of glycine for calibration. RM produced under accreditation to ISO 17025 and 17034
2015	Anal Bioanal Chem (2015) 407:3169–3180 DOI 10.1007/s00216-014-7926-1 RESEARCH PAPER **Calibration strategies for the determination of stable carbon absolute isotope ratios in a glycine candidate reference material by elemental analyser-isotope ratio mass spectrometry** **Philip J. H. Dunn · Dmitry Malinovsky · Heidi Goenaga-Infante**	Confirmation using EA-IRMS and redetermination of absolute isotope ratio of VPDB international measurement standard.

Limitations of the work

- Parent glycines enriched in ^{13}C and ^{12}C were not investigated for possible co-enrichment of H, N and O isotopes
  - Potential for molecular weights of the parent glycines to be outside of uncertainty bounds used in calculations (so uncertainty in final ratios may be underestimated)
  - Parent glycines sent to the USGS Stable Isotope Laboratory in Reston, Virginia for analysis
  - No significant enrichment found which would cause the molecular weights we used for the parent glycines to be invalid.
- With one reference material, calibration is not possible as it is preferable to use two or more RMs to allow scale span to be determined.
  - Suite of three glycines with isotopic compositions spanning the natural abundance range prepared as reference materials.

Acknowledgement:
Tyler Coplen and Haiping Qi at the USGS Reston SIL

Fully calibrated?	✓
Detailed uncertainty budget?	✓
RM available?	✓
CIAAW concerns addressed	✓

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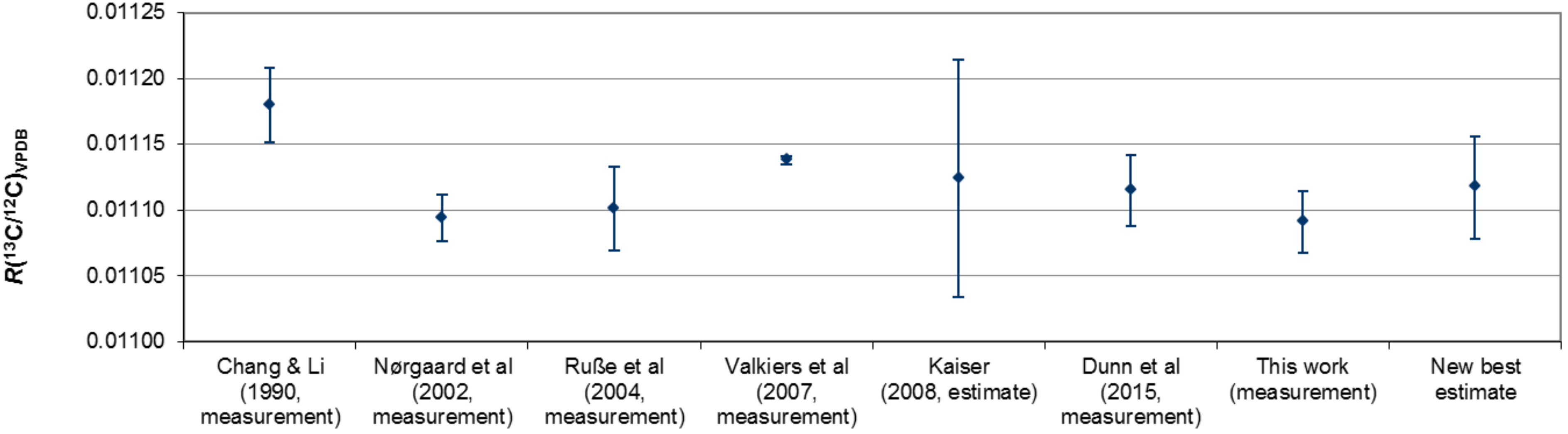
Development and characterisation of new glycine certified reference materials for SI-traceable $^{13}C/^{12}C$ isotope amount ratio measurements

D. Malinovsky,* P. J. H. Dunn,* G. Holcombe, S. Cowen and H. Goenaga-Infante

- CIAAW has recognised this work as a new best measurement of the isotopic abundance of carbon

What about VPDB?

$$\delta^{13}C = \frac{^{13}R_{sample}}{^{13}R_{standard}} - 1$$



- Similar approach now adopted by CIAAW but using a slightly different calculation approach to come up with their own best estimate (NIST Consensus Builder – available online)

Impacts of change to recommended absolute isotope ratio of VPDB

- Change to recommended ^{17}O correction algorithm
  - Impact on measurement of clumped isotopes
- Optical instrumentation
- Conversion of isotope delta to other quantities (absolute ratios, atom fractions, atomic weight)

- Submitted STELLAR project (EURAMET) is hoping to supply more independent measurements of this ratio to reduce the associated uncertainty significantly.

Summary

- LGC has worked towards measuring absolute isotope ratios traceable to the SI for a number of years
  - Achieved ISO/IEC 17025 accreditation for measurement by MC-ICP-MS
  - Produced four RMs under ISO/IEC 17034 accreditation
  - Re-determined the absolute isotope ratio of VPDB (the virtual international standard)
- This body of work has recently been recognised as the best measurement of the isotopic abundance of carbon by IUPAC CIAAW

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- Simon Cowen, Steve Ellison and the stats team
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- Ty Coplen and Haiping Qi at the USGS Reston Stable Isotope Laboratory