

SI Traceability for Vienna Peedee Belemnite

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What is Vienna Peedee belemnite (VPDB)?

- Vienna Peedee belemnite is the international measurement standard for carbon (and oxygens) **isotope delta** (δ) - a relative measure of **isotope ratio** (R) of a sample relative to a standard that is defined as follows:

$$\delta_{VPDB}(^{13}\text{C}/^{12}\text{C}) = \left(\frac{R_{\text{sample}}(^{13}\text{C}/^{12}\text{C}) - R_{VPDB}(^{13}\text{C}/^{12}\text{C})}{R_{VPDB}(^{13}\text{C}/^{12}\text{C})} \right)$$

- VPDB is hypothetical material that does not physically exist in material form, instead it is defined by the exact carbon isotope delta value assigned to the calcite reference material NBS 19 of $\delta_{VPDB}(^{13}\text{C}/^{12}\text{C}) = +1.95\text{‰}$ back in 1987.
- In 2006, the reference material LSVEC lithium carbonate was adopted as a second scale-defining international measurement standard for carbon isotope delta with exact $\delta_{VPDB}(^{13}\text{C}/^{12}\text{C}) = -46.6\text{‰}$.
- LSVEC was found to be unstable in terms of carbon isotopic composition in 2015.
- Characterisation studies for replacement carbonate reference materials produced by the IAEA and the USGS highlighted that measurements results traceable to only NBS 19 and those traceable to both NBS 19 and LSVEC were biased against each other – there were in fact two scales in concurrent use.
- This highlights the limitations of using scales defined by specific artifacts.

Importance of the isotopic composition of VPDB

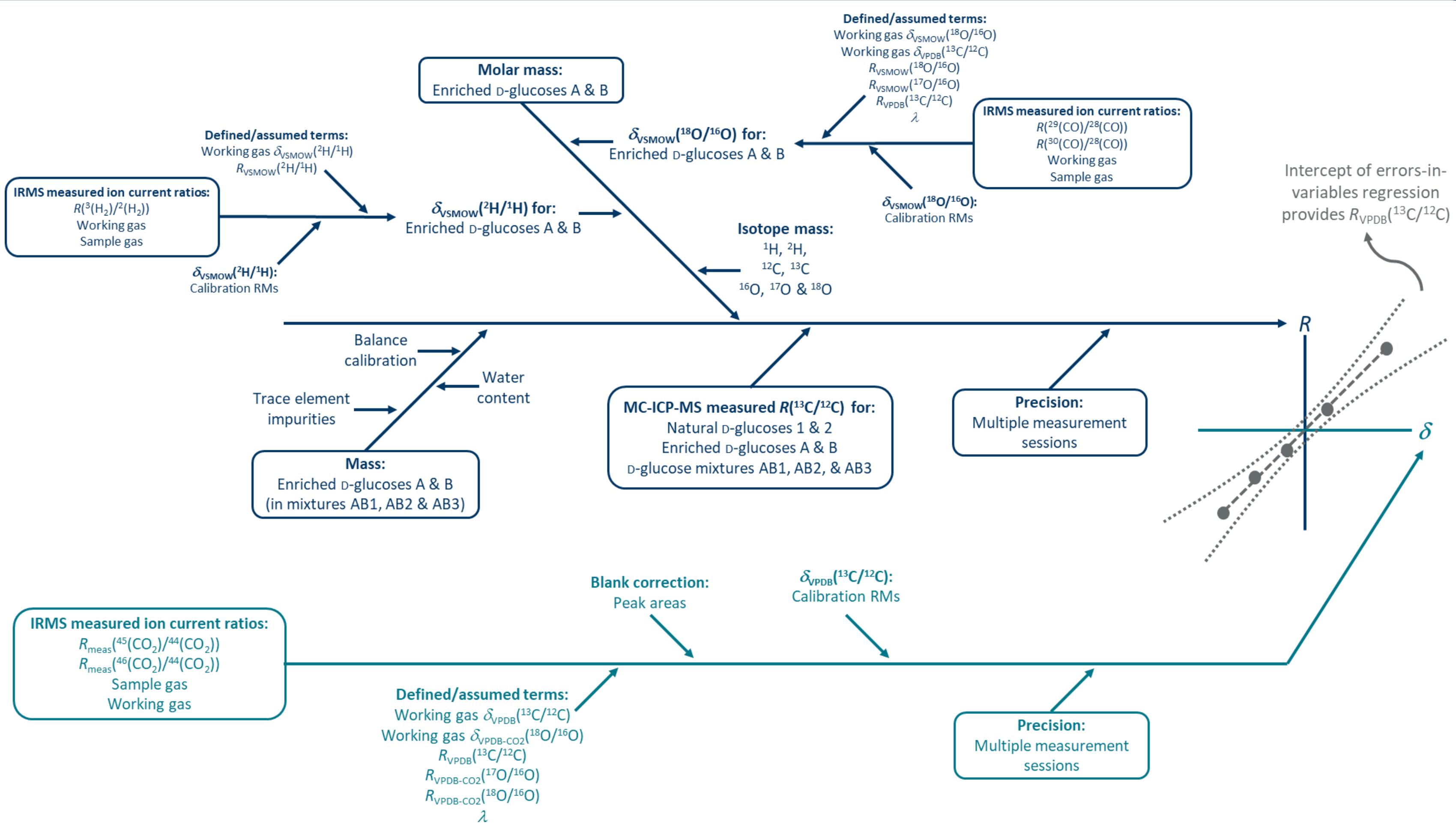
- Conversions between **isotope delta** and other quantities relating to carbon isotopic composition (isotope amount fraction, isotope ratio, atomic weight, etc).
- Data processing (“¹⁷O corrections,” “clumped” isotopic composition).
- Isotopic composition of VPDB is the link between the **isotope delta scales** and the International System of Units (SI), although, **isotope delta** is currently the subject of a traceability exception

Determination of the SI-traceable isotopic composition of VPDB

- Requires measurement of SI-traceable isotope ratios (R) as well as **VPDB-traceable isotope deltas** (δ) for several materials with differing carbon isotopic composition.
- Use errors-in-variables regression to obtain R when δ is exactly zero.

Improvements over previous methods

- Glucose rather than glycine as compound of choice (no need to consider N).
- Co-enrichment of H and O measured using an isotope ratio mass spectrometer with equal amplification on the necessary Faraday cups.
- The starting glucose materials happened to have significantly less co-enrichment of non-C elements
- Planning of weighing activities to minimise uncertainty while still producing sufficient amounts of solution with concentrations that could minimize the contribution of the blank.
- External validation of all instrumental measurements (MC-ICP-MS for R and EA-IRMS for δ) by participants in the EURAMET 19ENV05 STELLAR project.



Measurements of isotopic composition traceable to the SI

- Use a primary measurement method, or a reference material with SI-traceable isotope ratios (not isotope delta!) for calibration of instrumental measurement results.
- Can use a different element provided the differences in instrumental mass fractionation between the elements can be established reliably.
- Primary methods for SI-traceable isotope ratio fall into two categories
- Gravimetric mixtures of “pure” isotopes or enriched isotopologues
- Ab initio* methods

Gravimetric mixtures

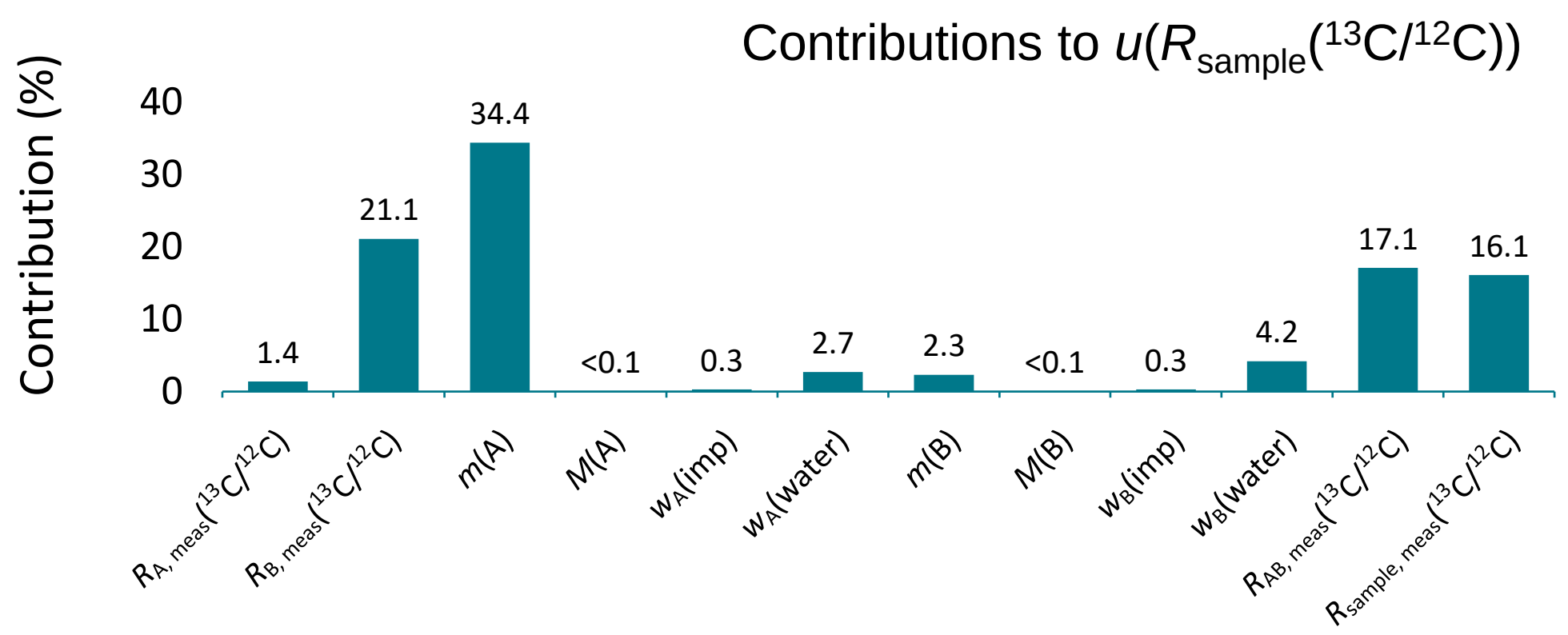
- Starting materials consisting of purified isotopes of an element, or isotopologues enriched in specific isotopes of an element are characterised for purity (trace elements, water content, co-enrichment of other isotopes)
- Mixtures of these starting materials are made gravimetrically.
- Measurement of the isotope ratio of the starting materials and mixtures allows instrumental mass fractionation to be determined and corrected for provided that mass fractionation is independent of isotopic composition (this is the case for MC-ICP-MS).

Previous studies

- Measurements used to determine SI-traceable isotope ratio generally by isotope ratio mass spectrometry (IRMS), some by MC-ICP-MS. Two *ab initio* methods also used: optical spectroscopy and the ¹³C satellites in 1H NMR.
- Variety of starting materials enriched in ¹²C and ¹³C including BaCO₃, CF₄, CO₂ & glycine used to prepare mixtures for calibration. External elements also used, including Xe, Kr, S and B.

Results

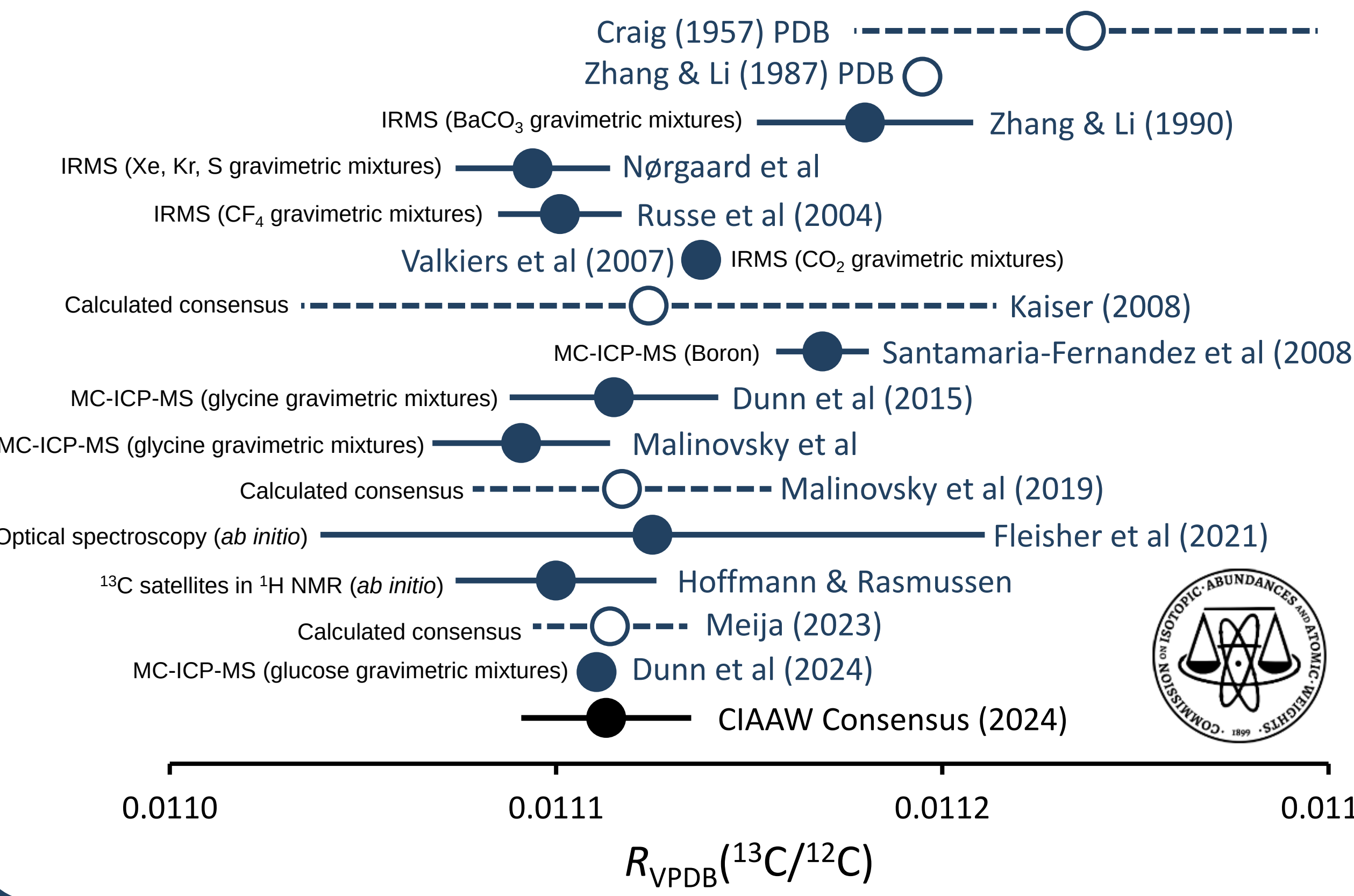
- Successful validation of all instrumental measurement results.
- Measurement uncertainty reduced by an order-of-magnitude over previous efforts using glycine.
- $R_{VPDB}(^{13}\text{C}/^{12}\text{C}) = 0.0111105 \pm 0.0000042$ (expanded uncertainty, $k = 2$)



- Largest contributing factors to measurement uncertainty in measured isotope ratios (R) were instrumentally-measured isotope ratios as well as the mass of the starting glucose enriched in ¹³C (glucose A).

Impact

- This work recently recognised by the IUPAC Commission on Isotopic Abundances and Atomic Weights (CIAAW) as the best mass spectrometric measurement of the isotopic composition of carbon from a single terrestrial sample, commonly known as the “IUPAC Best Measurement.”
- The CIAAW have also revised their recommended values for the isotopic composition of VPDB for the first time since 1990 for carbon and 2010 for oxygen.
- The carbon isotope ratio for VPDB is derived from a consensus considering all measurement results (filled symbols in plot below) rather than simply selecting the current best measurement.



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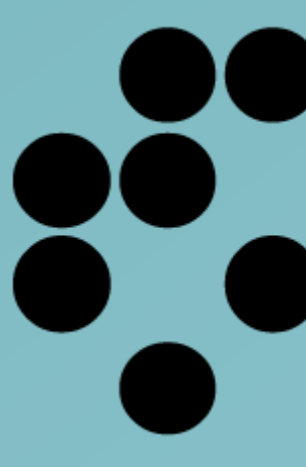
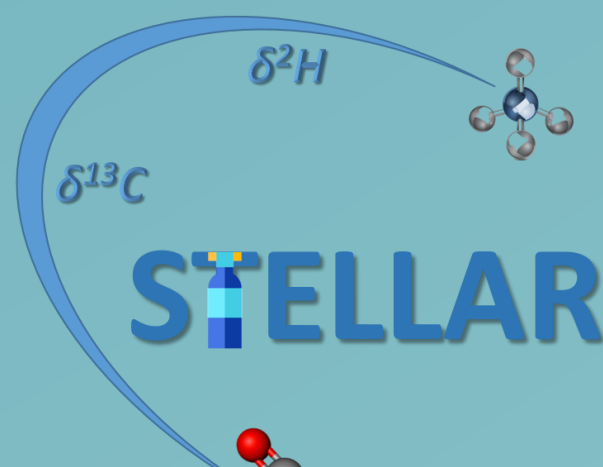
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