*Rapid Communications in Mass Spectrometry*

Check for updates

WILEY

Rapid Communications in Mass Spectrometry

**PERSPECTIVE** OPEN ACCESS

# Stable Isotope Reference Materials and Scale Definitions—Outcomes of the 2024 IAEA Experts Meeting

Federica Camin[1] | Dinka Besic[1] | Paul J. Brewer[2] | Colin E. Allison[3] | Tyler B. Coplen[4] | Philip J. H. Dunn[5] | Matthias Gehre[6] | Manfred Gröning[7] | Harro A. J. Meijer[8] | Jean-François Hélie[9] | Paola Iacumin[10] | Rebecca Kraft[11] | Bor Krajnc[12] | Steffen Kümmel[6] | Sangil Lee[13] | Juris Meija[14] | Zoltan Mester[14] | Joachim Mohn[15] | Heiko Moossen[16] | Haiping Qi[4] | Grzegorz Skrzypek[17] | Peter Sperlich[18] | Joelle Viallon[19] | Leonard I. Wassenaar[20] | Robert I. Wielgosz[19]

[1]Terrestrial Environmental Radiochemistry Laboratory, Division of Physical and Chemical Sciences, Department of Nuclear Sciences and Applications, International Atomic Energy Agency, Vienna, Austria | [2]National Physical Laboratory, Teddington, UK | [3]Commonwealth Scientific and Industrial Research Organisation, Aspendale, Victoria, Australia | [4]U. S. Geological Survey, Reston, Virginia, USA | [5]National Measurement Laboratory, LGC Limited, Teddington, UK | [6]Helmholtz Centre for Environmental Research GmbH, Leipzig, Germany | [7]Formerly at International Atomic Energy Agency, Vienna, Austria | [8]Centre for Isotope Research, University of Groningen, Groningen, Netherlands | [9]Geotop & Département des sciences de la Terre et de l'atmosphère, Université du Québec à Montréal, Montreal, Canada | [10]Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma, Parma, Italy | [11]National Institute of Standards and Technology, U. S. Department of Commerce, Gaithersburg, Maryland, USA | [12]Department of Environmental Sciences, Jožef Stefan Institute, Ljubljana, Slovenia | [13]Korea Research Institute of Standards and Science, Daejeon, The Republic of Korea | [14]Metrology Research Centre, National Research Council Canada, Ottawa, Canada | [15]Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland | [16]Max Planck Institute for Biogeochemistry, Jena, Germany | [17]West Australian Biogeochemistry Centre, School of Biological Sciences, The University of Western Australia, Perth, Australia | [18]National Institute of Water and Atmospheric Research Ltd, Wellington, New Zealand | [19]Bureau International des Poids et Mesures, Sèvres, France | [20]WasserCluster Lunz Biologische Station GmbH, Lunz am See, Austria

**Correspondence:** Federica Camin (f.camin@iaea.org)

**Received:** 8 October 2024 | **Revised:** 21 February 2025 | **Accepted:** 22 February 2025

**Keywords:** carbon | non-exchangeable hydrogen | oxygen | reference materials | stable isotope delta scales | VPDB

## ABSTRACT

The participants of the 12th International Atomic Energy Agency (IAEA) meeting on stable isotope reference materials reached a consensus, acknowledging the existence and use of two carbon isotope delta scales: the VPDB (Vienna Peedee belemnite) scale and the VPDB-LSVEC (LSVEC - lithium carbonate prepared by H. J. Svec). Conversion models between the two scales can be established and used but introduce uncertainty. A format for isotope delta scale definition was agreed upon and was used to define the two carbon isotope delta scales and the two main oxygen isotope delta scales, VSMOW-SLAP (Vienna Standard Mean Ocean Water–Standard Light Antarctic Precipitation) and VPDB. Confirmation or identification of a second-scale–defining point is still necessary for the nitrogen and sulfur isotope delta scales.

Efforts are encouraged to improve consistency among laboratories in the isotopic analysis of "non-exchangeable hydrogen" in bulk organic materials and oxygen in carbonates using the phosphoric acid reaction. Additional topics discussed include (1) need for improvement in reference materials for accurate greenhouse gas isotopic analyses; (2) reference materials under production by the IAEA, the US Geological Survey (USGS), and the US National Institute of Standards and Technology (NIST); (3) methods for value and uncertainty assignment of reference materials; and (4) calculation of carbon-13 isotope delta and oxygen-18 isotope delta of $CO_2$ measured by dual-inlet isotope ratio mass spectrometry.

## 1 | Introduction

The 12$^{th}$ International Atomic Energy Agency (IAEA) Meeting on the Development of Stable Isotope Reference Products was held in the Vienna International Centre from the 22nd to the 26th of January 2024. The first meeting (1967) was also held in Vienna, Austria, with subsequent meetings held every few years to address relevant developments in the field. A concurrent meeting was held to discuss the formal definitions and realization (i.e., how the scale definition is practically realized) of the isotope delta scales for several light elements. The role of these IAEA meetings is to guide IAEA's reference material (RM) program and the wider stable isotope community regarding using RMs for defining and realizing isotope delta scales and assisting analysts in normalizing their data properly. IAEA is also recognized as the custodian of stable isotope ratio measurement scales for the light elements (H, C, N, O, and S) [1]. Decisions on isotopic data normalization and on values (and uncertainties) of stable isotope RMs, especially of those defining and realizing isotope delta scales and other related topics, have been reached at these meetings [1–6].

The meeting brought together participants from the organizations producing light element stable isotope RMs, including the IAEA, the US National Institute of Standards and Technology (NIST), the US Geological Survey (USGS), the National Measurement Laboratory at LGC (NML at LGC), the National Research Council of Canada (NRC), the International Bureau of Weights and Measures (BIPM), the Executive Secretary for the Consultative Committee for Metrology in Chemistry and Biology (CCQM), chairs of Isotope Ratio and Gas Analysis working groups within CCQM, the past Chair and members of the International Union of Pure and Applied Chemistry (IUPAC) Commission on Isotopic Abundances and Atomic Weights (CIAAW), representatives of metrology organizations, and other internationally recognized experts in stable isotope analysis and application.

The main objectives of the meeting were to discuss the state-of-the-art on the following points and, when necessary, reach (or re-establish) consensus and decide on:

- Definition and realization of isotope delta scales of light elements, with focus on carbon and oxygen isotope delta scales.
- Requirements and future focus on RMs for analyses of stable isotope ratios in greenhouse gases, inorganic matrices, and organic matrices.
- Best practices for the characterization (value assignment and uncertainty assessment) of stable isotope RMs according to ISO 17034:2016 [7].
- Challenges in defining and realizing carbon and oxygen stable isotope scales via carbonates reacted with phosphoric acid to evolve carbon dioxide.
- Challenges in the stable isotope ratio analysis of non-exchangeable hydrogen in organic materials.
- Analysis of data obtained from dual-inlet isotope ratio mass spectrometry (DI-IRMS).

This article provides consensus outcomes, namely, the agreed template for isotope delta scale definition (Section 2), the consensus about the carbon isotope delta scale and the definition of VPDB and VPDB-LSVEC scales (Section 3), and the definitions of the two main oxygen isotope delta scales (Section 4). The article also highlights isotope scale definition and realization (Section 2) and nitrogen and sulfur isotope delta scales (Section 5) and briefly presents topics discussed at the meeting, including RMs under production, the need for new RMs for greenhouse gases analysis, approaches for the value assignment and uncertainty assessment of RMs, isotopic analysis of non-exchangeable hydrogen in organic materials, the carbonate phosphoric acid reaction, and the calculation of delta values using DI-IRMS (Section 6).

## 2 | Isotope Delta Scale Definition and Realization

The necessity of uniform nomenclature, definition, terminology, and vocabulary related to isotope delta values and scales was confirmed. In relation to these needs, there is an ongoing IUPAC project (2023-014-2-200) that is aimed at providing IUPAC recommendations for terminology and definitions of quantities relating to isotopic analyses.

To express isotope delta value measurements against a given scale, the participants agreed that it is necessary to have a commonly agreed upon definition for the scale and develop methods to realize that scale in practice through the assignment of consensus isotope delta values to specific materials that are consistent with the scale definition. An isotope delta scale is defined by taking a fixed numerical consensus delta value (without uncertainty) of a material, selected by international agreement. This definition determines one point in the delta scale (often but not always the zero point). Some isotope delta scales are defined by two distinct points. Often, the scale-defining material/s gives/give the name to the scale. Realizing the isotope delta scale means putting the scale definition into practice by using as calibrants one or more RMs with assigned values and associated uncertainty, which are consistent with the definition of the scale. As indicated in the document traceability exception for delta value isotope ratio measurement, approved by the International Committee for Weights and Measures (CIPM) in March 2015 [8], these materials are listed, published, and maintained by IUPAC (currently by Brand et al. [9]).

A format for isotope delta definitions was proposed and agreed upon during the meeting. It follows the template for defining the International System of Units (SI) in the SI Brochure [10]. The format proposed is based on a short text that defines the scale and is accompanied by explanatory notes. The short text includes the name of the scale, the specific isotope ratio, the symbol for the isotope delta, the fixed numerical isotope delta values for all RMs that define the scale and the identity of the zero point. For instance, for a scale with a single defining point, the text is as follows: The [name of the scale] scale for the [name of isotope] isotope delta value, expressed as $\delta$([symbol of numerator isotope]), is defined by taking the fixed numerical value of [number] for the $\delta$([symbol of numerator isotope]) of the [name of RM] RM, when expressed relative to [name of the scale]. Examples of isotope scale definitions following this agreed format are reported in Sections 3 and 4. It is expected that all internationally agreed isotope delta scales will have similar formal definitions which will be drafted and agreed upon by participants in meetings, such as the IAEA meeting, and then submitted as resolutions or publications to be endorsed by the CIPM and IUPAC CIAAW and made freely available for reference. Changes to the definition text, in particular the adoption or modification of fixed points, will establish a new scale that will require a new name to differentiate it from previous scales. Notes providing guidance related to a scale definition can be modified without the need to establish a new scale definition.

In line with these efforts, a previous IAEA meeting resolved to provide a document on the main concepts surrounding the isotope delta values [6] and isotope delta scales. In this regard, a second draft of the IUPAC Technical Report titled "International Isotope Delta Scales," sponsored by the IUPAC Inorganic Chemistry Division Committee and coauthored by many participants of this meeting, was presented at this meeting.

The progress of the IUPAC project on absolute ratios of RM was also presented, with a proposal of revision of the $R(^{13}\mathrm{C}/^{12}\mathrm{C})$ of VPDB, recently published [11].

## 3 | Carbon Isotope Delta Scale

### 3.1 | Carbon Isotope Delta Scale Background

The carbon VPDB scale was initially defined using NBS 19 calcite [12] with an assigned stable carbon-13 isotope delta value, $\delta(^{13}\mathrm{C})$, of +1.95‰ [13]. In this work, the expression of the quantity carbon isotope delta follows Skrzypek et al. [6]. Alternative expressions for the quantity include $\delta(^{13}\mathrm{C}/^{12}\mathrm{C})$ and more commonly $\delta^{13}\mathrm{C}$, following guidelines published in *Rapid Communications in Mass Spectrometry* as a protocol [6, 14, 15].

In 2006, the lithium carbonate RM, LSVEC, was introduced and described as a second-scale–defining point by IUPAC, supplementing NBS 19, to define the $\delta(^{13}\mathrm{C})$ scale [16, 17]. To identify measurement results reported on this scale, the notation $\delta(^{13}\mathrm{C})_{\mathrm{VPDB\text{-}LSVEC}}$ was commonly used [9].

In 2015, LSVEC was found to be unsuitable as a RM because its $\delta(^{13}\mathrm{C})$ value increased (became less negative) as it absorbed $\mathrm{CO}_2$ from the air [18]. Consequently, the CIAAW, after discussions during its 2017 meeting in Groningen (NL), issued a press release stating that LSVEC is no longer recommended for carbon isotope analysis [19]. As the lithium isotope ratio is not affected by the absorption of $\mathrm{CO}_2$, LSVEC is still suitable for calibration of lithium stable isotope measurements and still forms the zero point of the lithium isotope delta scale [20].

Since then, IAEA-610, IAEA-611, IAEA-612, and USGS44 reagent calcium carbonates have been introduced to enable measurements to be made traceable to the VPDB and/or VPDB-LSVEC scales. Currently, there are internationally recognized RMs traceable to NBS 19 alone (VPDB scale) and RMs traceable to VPDB-LSVEC scale.

These changes over the last few years have led to ongoing discussions on possible solutions to "the LSVEC problem" [21] and whether the two carbon isotope scales (VPDB and VPDB-LSVEC) are indeed two different measurement scales or simply different realizations of the same scale. The fact that using either one or both scale-defining RMs could result in different measurement values, led the participants to conclude that two different scales for $\delta(^{13}\mathrm{C})$ exist de facto.

The relationship between the two scales can be expressed by a mathematical equation allowing simple conversion of the results from one scale to the other [22]. Meeting participants have provided additional experimental results to supplement the equation Hélie et al. [22] established. However, the simple conversion proposed by Hélie et al. may need adjustments, because the isotope delta values assigned to IAEA-610, IAEA-611, and IAEA 612 [23] and to USGS44 [24] on the VPDB scale are not quite in agreement (see discussion below).

During the meeting, participants discussed three main possible solutions to "the LSVEC problem" mentioning possible substitutes of the LSVEC material as scale-defining materials, as described in details in Dunn and Camin [21]. Three possible solutions were identified, and pros and cons were discussed: [21] (1) to maintain only an unchanged VPDB-LSVEC scale, using another RM instead of LSVEC for its realization; (2) to maintain only the VPDB scale and remove LSVEC entirely; and (3) do not favour one scale over the other but maintain and recognize the existence of the two different scales, VPDB and VPDB-LSVEC.

The participants reached a consensus in acknowledging the existence and use of two carbon isotope delta scales with the following names:

- VPDB
- VPDB-LSVEC

The participants agreed on the definitions of the two scales in Sections 3.2 and 3.3 according to the format described in Section 2.

### 3.2 | VPDB Carbon Isotope Delta Scale Definition

The VPDB scale for the carbon-13 isotope delta value, expressed as $\delta(^{13}\mathrm{C})$, is defined by taking the fixed numerical value of +0.00195 for the $\delta(^{13}\mathrm{C})$ of the NBS 19 RM, when expressed relative to VPDB.

Notes

1. The quantity isotope delta is dimensionless and has the unit one. It is common practice to express numerical values of isotope delta, when multiplied by 1000, using the symbol permille (‰): For example, the consensus $\delta(^{13}\mathrm{C})$ value of NBS 19 is +1.95‰.
2. VPDB stands for Vienna Peedee belemnite.
3. VPDB is a virtual material; it does not and has not existed in material form. Its $\delta(^{13}\mathrm{C})$ value is exactly 0 on the VPDB scale.
4. The values of the $^{13}\mathrm{C}/^{12}\mathrm{C}$ isotope number ratio (commonly shorted to isotope ratio) [14] for the VPDB virtual material

and $^{17}O/^{16}O$ and $^{18}O/^{16}O$ isotope ratios in the $CO_2$ gas that would be liberated from VPDB in reaction with concentrated phosphoric acid at 25°C have been measured. Values currently recommended by IUPAC for these quantities are as follows:

$R(^{13}C/^{12}C,\ \mathrm{VPDB}) = 0.011113 \pm 0.000022$ (95% confidence level)

$R(^{17}O/^{16}O,\ \mathrm{VPDB\text{-}CO_2}) = 0.0003907 \pm 0.0000012$

$R(^{18}O/^{16}O,\ \mathrm{VPDB\text{-}CO_2}) = 0.00208839 \pm 0.00000092$

$\lambda = 0.528$ (assumed exact)

These values have been endorsed by the CIAAW in 2024 [25] and replace the recommendation of Brand, Assonov, and Coplen [26].

5. Carbonate RMs, such as NBS 19 which is quarantined [9], or IAEA-603 [27], that can be used instead of NBS 19, provide a means for analysts to realize the VPDB scale in practice. To achieve reliable measurements on the VPDB scale, IUPAC recommends the use of at least two RMs whose values have been determined relative to VPDB to minimize common sources of instrument measurement bias [28]. RM producers should demonstrate that their assigned values and the associated uncertainties on such RMs are consistent with the VPDB scale definition and with values and uncertainties of other RMs intended for the same purpose.
6. When reporting their measurement results, users should follow the minimum requirements established by IUPAC [6].
7. Carbon isotope delta values reported on the VPDB and VPDB-LSVEC scales can differ. Differences between delta values reported on the VPDB and VPDB-LSVEC scales range from +0.14‰ to +0.30‰ [22, 24] for materials with carbon isotope delta values around −45‰ and are negligible (below current analytical combined uncertainty) at carbon isotope delta values close to zero. Conversion models between the two scales can be established and used but will introduce uncertainty [22].

### 3.3 | VPDB-LSVEC Carbon Isotope Delta Scale Definition

The VPDB-LSVEC scale for the carbon-13 isotope delta value, expressed as $\delta(^{13}C)$, is defined by taking the fixed numerical value of +0.00195 for $\delta(^{13}C)$ of the NBS 19 RM and −0.0466 for the $\delta(^{13}C)$ of the LSVEC RM, when expressed relative to VPDB.

Notes

1. The quantity isotope delta is dimensionless and has the unit one. It is common practice to express numerical values of isotope delta, when multiplied by 1000, using the symbol permille (‰).
2. VPDB stands for Vienna Peedee belemnite and LSVEC is a lithium carbonate originally prepared by H.J. Svec [20, 29, 30] for use as a stable lithium isotope RM.
3. VPDB is a virtual material; it does not and has not existed in material form. Its $\delta(^{13}C)$ is exactly 0 on the VPDB scale.
4. The values of the $^{13}C/^{12}C$ isotope number ratio (commonly shorted to isotope ratio) [14] for the VPDB virtual material and $^{17}O/^{16}O$ and $^{18}O/^{16}O$ isotope ratios in the $CO_2$ gas that would be liberated from VPDB in reaction with concentrated phosphoric acid at 25°C have been measured. Values currently recommended by IUPAC for these quantities are as follows:

   $R(^{13}C/^{12}C,\ \mathrm{VPDB}) = 0.011113 \pm 0.000022$ (95% confidence level)

   $R(^{17}O/^{16}O,\ \mathrm{VPDB\text{-}CO_2}) = 0.0003907 \pm 0.0000012$

   $R(^{18}O/^{16}O,\ \mathrm{VPDB\text{-}CO_2}) = 0.00208839 \pm 0.00000092$

   $\lambda = 0.528$ (assumed exact)

   These values have been endorsed by the CIAAW in 2024 [25] and replace the recommendation of Brand, Assonov, and Coplen [26].

5. Carbonate RMs, such as NBS 19 which is quarantined [9], or IAEA-603 [27], that can be used instead of NBS 19, provide a means for analysts to realize the VPDB-LSVEC scale in practice. Due to reported material instability, the lithium carbonate certified RM, LSVEC, is no longer recommended for realizing the VPDB-LSVEC scale. Other RMs whose values have been determined relative to the VPDB-LSVEC scale continue to provide accurate representations of the VPDB-LSVEC scale [9, 24, 31–34]. To achieve reliable measurements on the VPDB-LSVEC scale, IUPAC recommends the use of at least two RMs whose values have been determined relative to VPDB-LSVEC to minimize common sources of instrument measurement bias [28]. RM producers should demonstrate that their assigned values and uncertainties on such RMs are consistent with the scale definition and with values and uncertainties for other RMs intended for the same purpose. The internal consistency of secondary RM values assigned on the VPDB-LSVEC scale has been demonstrated in the interlaboratory comparison CCQM-P212 [35].
6. When reporting their measurement results, users should follow the minimum requirements established by IUPAC [6].
7. Differences between delta values reported on the VPDB and VPDB-LSVEC scales range from +0.14‰ to +0.30‰ [22, 24] for materials with carbon isotope delta values around −45‰ and are negligible (below current analytical combined uncertainty) at carbon isotope delta values close to zero. Conversion models between the two scales can be established and used but will introduce uncertainty [22].

### 3.4 | Recommendations for the Carbon Isotope Delta Scales

A strategic plan needs to be implemented to guarantee that the achieved consensus is communicated to the scientific communities. The existence of the two scales will be acknowledged by the new IUPAC Technical Report on stable isotope delta scale RMs, listing values and uncertainties of the RMs suitable for isotope delta scale realization. The current report [9] is under revision by the CIAAW Subcommittee on Stable Isotope Reference Material Assessment (IUPAC Project 2014-002-1-200).

Those measuring $\delta(^{13}C)$ values should state the isotope delta values of RMs used following the minimum requirements established by IUPAC [6] and whether they are reporting $\delta(^{13}C)$ values on the VPDB scale or the VPDB-LSVEC scale. Users should ensure that in one calibration they only use values for RMs assigned on one scale.

As the maximum reported difference (VPDB minus VPDB-LSVEC) is +0.3‰ for materials with carbon isotope delta values around −45‰ and negligible (below current analytical combined uncertainty) at carbon isotope delta values close to zero, the differences between the VPDB and VPDB-LSVEC scales can be insignificant for those making measurements with uncertainties greater than the scale differences and analyzing values less negative than −45‰.

Producers of RMs should clearly indicate on which scale they have assigned their products a value based on the RMs used for calibration. Isotope delta values can be assigned on both scales, which should be unambiguously indicated.

When the VPDB-LSVEC scale was established, LSVEC lithium carbonate was directly analyzed but the material's heterogeneity and instability were not accounted for. Instead, an exact carbon isotope delta value was assigned to the LSVEC material; hence, an additional component of uncertainty may be required for every material traceable to the RMs characterized in that original study [36].

For both scales, propagation of uncertainties assigned to isotope delta values of RMs used for calibration should be assured by adopting the principles of the GUM [37].

In addition to NBS 19 which is quarantined [9], or IAEA-603 [27] that can be used instead of NBS 19, the RMs IAEA-610, IAEA-611, and IAEA-612 can be used to calibrate measurement results to the VPDB carbon isotope delta scale. The RM USGS44 has assigned $\delta(^{13}C)$ values on both scales and may also be used for calibration to either VPDB or VPDB-LSVEC scale [24, 38] Participants recommended confirming and consolidating the published values of IAEA-610, IAEA-611, and IAEA-612 [23] and USGS44 [24] by assessing these materials together and with other carbonate RMs.

## 4 | Oxygen Isotope Delta Scales

### 4.1 | Oxygen Isotope Delta Scale Background

As described in a sequence of IAEA reports over the years [5, 13] and by Coplen [39], two main oxygen isotope delta scales are currently available:

- The VSMOW-SLAP (Vienna Standard Mean Ocean Water–Standard Light Antarctic Precipitation) scale, defined by water RMs and typically used for measurement of $\delta(^{18}O)$ and $\delta(^{2}H)$ of water or hydrogen- or oxygen-bearing materials.
- The VPDB scale, defined by a carbonate RM and used for measurement of $\delta(^{13}C)$ and $\delta(^{18}O)$ of carbonates and carbon dioxide [39].

In addition, a third scale, defined by air-$O_2$ gas [9], is used by a small number of groups in a specific application and due to its limited use, it is not further described here.

Notably, for both main oxygen isotope delta scales, the substances defining them (water and carbonates) are not the substances on which measurements using IRMS are performed, which in both cases are $CO_2$. As a result, the two scales can be coupled through the comparison of the $\delta(^{18}O)$ in $CO_2$ that is equilibrated with VSMOW (VSMOW-$CO_2$) and $\delta(^{18}O)$ in $CO_2$ produced from a RM whose oxygen-18 isotope delta value has been determined on the VPDB scale by reaction with concentrated phosphoric acid at 25°C (VPDB-$CO_2$). The difference in the numerical values of $\delta(^{18}O)$ between these two carbon dioxide gases is small, with the $\delta(^{18}O)$ of VSMOW-$CO_2$ being slightly negative with respect to VPDB-$CO_2$. Values are rarely reported in the literature and vary between −0.25‰ and −0.32‰ [40–42]. The latest published value of −0.28‰ is based on a critical overview of these results [43].

The original idea behind both scales is that, as long as the interaction with $CO_2$ is performed following strict guidelines, $CO_2$ from samples of water and carbonate should be comparable to the $CO_2$ from the RMs in precisely the same way as the samples of water and carbonate would compare to the RMs themselves, and the oxygen isotopic fractionation between the materials and the $CO_2$ would have no effect on the results. However, suppose other materials, such as atmospheric $CO_2$, are analyzed, the isotopic fractionation between sample and RMs is not equivalent. In these cases, values need to be expressed with respect to VSMOW-SLAP-$CO_2$ or VPDB-$CO_2$ or values of oxygen isotopic fractionation factors used in data evaluations need to be specified.

For pure water, optical spectroscopy is commonly used for stable oxygen isotope ratio measurements, directly on water. For those measurements, the $CO_2$ equilibration with its isotopic fractionation is no longer relevant. For carbonates, however, direct measurements remain complicated.

The preparation of $CO_2$ from calcites using oversaturated phosphoric acid is a potentially error-prone process: it involves kinetic fractionation, and it is sensitive to the reaction temperature, the presence of water in the system, the saturation level of the phosphoric acid, and the $\delta(^{18}O)$ of the water in the phosphoric acid. Furthermore, producing and keeping reliable and stable calcium carbonate RMs for $\delta(^{18}O)$ are difficult due to possible interaction with moisture and atmospheric $CO_2$. For example, the IAEA-610, IAEA-611, and IAEA-612 series and USGS44 are not recommended for use for $\delta(^{18}O)$ measurements. Therefore, it was agreed more than three decades ago to define the VSMOW-SLAP scale as the primary oxygen isotope delta scale (CIAAW meeting in Lisbon, Portugal, 1993) [39] and subsequently define the VPDB-$CO_2$ scale in terms of the VSMOW-SLAP scale [39].

### 4.2 | VSMOW-SLAP Oxygen Isotope Delta Scale Definition

The VSMOW-SLAP scale for oxygen-18 isotope delta value, expressed as $\delta(^{18}O)$, is defined by taking the fixed numerical value of 0 for $\delta(^{18}O)$ value of the VSMOW RM and −0.0555 for the $\delta(^{18}O)$ value of the SLAP RM, when expressed relative to VSMOW.

Notes

1. The quantity isotope delta is dimensionless and has the unit one. It is common practice to express numerical values of isotope delta using the symbol permille (‰).
2. VSMOW stands for Vienna Standard Mean Ocean Water, and SLAP standards for Standard Light Antarctic Precipitation.
3. While limited amounts of the original VSMOW and SLAP reference waters may still be available in some laboratories, to enable continuous wide distribution of RMs for the VSMOW-SLAP scale realization, VSMOW and SLAP have been replaced, by VSMOW2 and SLAP2, respectively, and have identical $\delta(^{18}O)$ values, but with an uncertainty with respect to VSMOW and SLAP.
4. The $^{18}O/^{16}O$ and $^{17}O/^{16}O$ isotope ratios of VSMOW have been based on measurements by Baertschi [44] and Li et al [45], respectively. The IUPAC recommended values for these quantities are as follows: [25]

   $R(^{18}O/^{16}O, \text{VSMOW}) = 0.0020052 \pm 0.0000009$ (95% confidence level)

   $R(^{17}O/^{16}O, \text{VSMOW}) = 0.0003824 \pm 0.0000012$

5. By equilibrating VSMOW with $CO_2$ gas, at 25°C and for a time sufficiently long to establish isotopic equilibrium, VSMOW-$CO_2$ is created, taking into account the masses of oxygen in the $CO_2$ gas and the water [46]. The $R(^{18}O/^{16}O)$ and $R(^{17}O/^{16}O)$ isotope ratios of this $CO_2$ are higher than those in VSMOW due to equilibrium isotopic fractionation. For $^{17}O$ measurements, no consensus value has been achieved. For $^{18}O$ measurements, based on experiments by various authors [13, 40, 43, 47], the following value is now taken for the isotopic fractionation:

   $R(^{18}O/^{16}O, \text{VSMOW-CO}_2)/R(^{18}O/^{16}O, \text{VSMOW}) = 1.0412$ (commonly accepted value, assumed exact).

   In practice, the oxygen atoms in the original $CO_2$, with their specific isotope ratio, contribute to the total initial oxygen pool and thus will have a nonnegligible influence on the isotopic composition of the equilibrated $CO_2$ gas. The smaller the relative amount of $CO_2$ is with respect to the water, the smaller the correction needed is for this effect (e.g., [42, 48]).

6. If SLAP is treated in the same way as VSMOW, the $\delta(^{18}O)$ value of the formed SLAP-$CO_2$ is −0.0555 with respect to VSMOW-$CO_2$ (see also Figure 2 in Hillaire-Marcel et al.) [43].
7. RMs, such as VSMOW2 and SLAP2, provide a means to realize the VSMOW-SLAP scale. To achieve reliable measurements on the VSMOW-SLAP scale, IUPAC recommends the use of at least two RMs whose values have been determined relative to VSMOW-SLAP to minimize common sources of instrument measurement bias [28]. RM producers should demonstrate that their assigned values and uncertainties on such RMs are consistent with the scale definition and with values and uncertainties for other RMs intended for the same purpose.
8. When reporting their measurement results, users should follow the minimum requirements established by IUPAC [6].
9. The $\delta(^{18}O)$ value of SLAP with respect to VSMOW has been based on consensus [49] and might well not be the true value [50]. Therefore, oxygen isotope delta values reported on the VSMOW-SLAP scale and those reported using VSMOW only might differ.

### 4.3 | VPDB and VPDB-$CO_2$ Oxygen Isotope Delta Scale Definitions

The VPDB scale for oxygen-18 isotope delta value, expressed as $\delta(^{18}O)$, is defined by taking the fixed numerical value of −0.0022 for $\delta(^{18}O)$ of the NBS 19 RM, when expressed relative to VPDB. The VPDB-$CO_2$ scale for oxygen-18 isotope delta value, expressed as $\delta(^{18}O)$, is defined by taking the fixed numerical value of −0.0022 for $\delta(^{18}O)$ of the $CO_2$ gas liberated from the NBS 19 RM in reactions with oversaturated phosphoric acid at 25°C, when expressed relative to VPDB-$CO_2$.

Notes

1. The quantity isotope delta is dimensionless and has the unit one. It is common practice to express numerical values of isotope delta using the symbol permille (‰).
2. VPDB stands for Vienna Peedee belemnite.
3. VPDB is a virtual material; it does not and has not existed in material form. The $\delta(^{18}O)$ value of VPDB is 0 on the VPDB scale. The most recent $\delta(^{18}O)$ value of VPDB is taken to be 0.03092 on the VSMOW-SLAP scale (assumed exact) [9, 51].
4. Based on experiments by various authors [13, 40, 43, 47, 51], the following value is most commonly accepted for the oxygen-18 isotopic fractionation of calcite and is also recommended by IUPAC:

   $R(^{18}O/^{16}O, \text{VPDB-CO}_2)/R(^{18}O/^{16}O, \text{VPDB}) = 1.01025$ (commonly accepted value, assumed exact).

5. All $\delta(^{18}O)$ values on the VPDB and VPDB-$CO_2$ scales can be converted to $\delta(^{18}O)$ values on the VSMOW-SLAP scale or relative to VSMOW-SLAP-$CO_2$ scale using the oxygen isotopic fractionation factors listed below and the established difference between VSMOW-$CO_2$ and VPDB-$CO_2$. These values are subject to remeasurement and follow from the values mentioned above [51] (see also Figure 2 in

Hillaire-Marcel et al. [43]). Current equations for scale conversion for material X are as follows:

$\delta(^{18}O,\ X)_{VSMOW\text{-}SLAP} = 1.03092\ \delta(^{18}O,\ X)_{VPDB} + 30.92‰$ (commonly accepted value, assumed exact) [51].

$\delta(^{18}O,\ X)_{VSMOW\text{-}SLAP} = 1.04149\ \delta(^{18}O,\ X)_{VPDB\text{-}CO2} + 41.49‰$ (commonly accepted value, assumed exact) [43].

$\delta(^{18}O, X)_{VSMOW\text{-}SLAP\text{-}CO2} = 1.00029\ \delta(^{18}O, X)_{VPDB\text{-}CO2} + 0.29‰$ (commonly accepted value, assumed exact) [43].

When appropriate, users should state the conversion equation they use in their publications. Uncertainties of these consensus values have not yet been evaluated.

6. Because the definition of the scale does not contain a second RM with a stable, more negative value for $\delta(^{18}O)$, $CO_2$ equilibrated with the SLAP RM shall be used, with a defined $\delta(^{18}O)$ value of −0.05576, when expressed relative to VPDB-$CO_2$. The value of −0.05576 is a combination of −0.0555 (SLAP vs. VSMOW) and −0.00028 (VSMOW-$CO_2$ vs. VPDB-$CO_2$).
7. To achieve reliable measurements on the VPDB scale, IUPAC recommends the use of at least two RMs whose values have been determined relative to VPDB to minimize common sources of instrument measurement bias [28]. While there is no second scale-defining point, there are several RMs with oxygen isotope delta values more negative than NBS 19. The two RMs should have the same chemical composition as the samples to avoid bias due to the different chemical compositions of the carbonates [52]. RM producers should demonstrate that their assigned values and the associated uncertainties on such RMs are consistent with the VPDB scale definition (including the requirement for SLAP) and with values and uncertainties of other RMs intended for the same purpose.
8. When reporting their measurement results, users should follow the minimum requirements established by IUPAC [6].

## 5 | Nitrogen and Sulfur Isotope Delta Scales

The nitrogen isotope delta scale is based on Air-$N_2$ with a $\delta(^{15}N)$ value of 0 [53]. For practical reasons, IAEA-N-1 ($\delta(^{15}N)_{Air\text{-}N2} = +0.43‰ \pm 0.07‰$) is commonly used as a solid RM for realizing the Air-$N_2$ isotope delta scale, and USGS32 ($\delta(^{15}N)_{AIR\text{-}N2} = +180‰$) has been used as a second anchor for scale realization to normalize $\delta(^{15}N)$ data, based on results in Böhlke and Coplen [54]. Reported $\delta(^{15})N$ values for many other commonly used inorganic and organic isotopic RMs are consistent with those data [31, 32, 54, 55].

The sulfur isotope delta scale is defined by assigning a fixed $\delta(^{34}S)$ numerical value of −0.3‰ to IAEA-S-1 expressed relative to VCDT [56]. During the 8th IAEA Advisory Group Meeting on Future Trends in Stable Isotope Reference Materials, which took place in 2000 [3], it was recommended that IAEA-S-2 or IAEA-S-3 silver sulfide RMs be used with IAEA-S-1 for the VCDT scale realization.

The participants concurred on the necessity to verify the definition and realization of the nitrogen and sulfur isotope delta scales, including confirming or identifying the second anchors where necessary. This will be a topic for the next IAEA meeting.

## 6 | Other Topics Discussed

### 6.1 | Greenhouse Gas RMs

The session focused on $CO_2$, $CH_4$, and $N_2O$ gas RMs for underpinning measurements of atmospheric source apportionment. It presented a calibration scheme for methane isotope ratio analyzers and IRMS developed at National Institute of Water and Atmospheric Research Ltd. (NIWA) [57–59].

Progress from the SIRS (16ENV06) and STELLAR (19ENV05) projects funded by the European Union's Horizon 2020 research and innovation program was reported regarding developments on isotopic $CO_2$ and $CH_4$ gas RMs for underpinning measurements performed using commercial spectroscopy [60].

An update on the role of the central calibration laboratory at MPI-BGC (Max Planck Institute for Biogeochemistry) focused on the challenges in maintaining the World Meteorological Organization (WMO) scale for the $CO_2$ isotope ratio. Discussions led to considering parallels to the infrastructure and developments for the $CO_2$ amount fraction scale, and collaboration with the community focused on amount fraction scale was encouraged.

The BIPM reported on the comparison of capabilities to assign $\delta(^{13}C)$ and $\delta(^{18}O)$ values in $CO_2$ in air standards (CCQM-P239), which follows the study on pure $CO_2$ gases (CCQM-P204) [61]. The CCQM-P204 study provided invaluable insights into the traceability chains and RMs currently employed to achieve these measurement results. The results confirmed the previously reported difference between the VPDB and VPDB-LSVEC scale. Follow-on studies will be aimed at comparing the uncertainties and levels of consistency of applying the phosphoric acid/carbonate reference system for value assigning $\delta(^{13}C)$ and $\delta(^{18}O)$ values in pure $CO_2$ gas.

Research on RMs of both pure and atmospheric $CO_2$/$CH_4$ isotopes traceable to both SI and delta scales was presented by Korea Research Institute of Standards and Science (KRISS). KRISS prepared isotope ratio RMs gravimetrically using $CO_2$ gases that are enriched in $^{13}CO_2$ (and depleted in $^{12}CO_2$) and enriched in $^{12}CO_2$ (and depleted in $^{13}CO_2$). There materials were used for measuring (absolute) isotope ratios of the VPDB scale, using IRMS with a batch inlet, traceable to the SI. In this batch inlet, sample gas from a temperature-controlled 2-L sample vessel is introduced into an ion source by molecular flow through a gold foil for quantitative analysis, ensuring reproducible sensitivity and reliable calibration [62, 63]. Preliminary results of $R(^{13}C/^{12}C, VPDB)$ were consistent with other previously reported values [11].

A report on the status of nitrous oxide RMs and calibrations developed within the SIRS (16ENV06) project was presented by Swiss Federal Laboratories for Materials Science and Technology (Empa): two secondary pure $N_2O$ RMs were introduced by the

USGS in 2018: USGS51 and USGS52 [64, 65]. Additional secondary pure $N_2O$ RMs were produced within the EURAMET project SIRS, value assigned by several laboratories [66], and subsampled by USGS, to facilitate two-point calibration by end-users. The isotope delta values of novel $N_2O$ RMs are currently under discussion. Efforts have been made to produce $N_2O$ in air RMs in collaboration with metrology institutes (National Physical Laboratory (NPL)) and commercial producers.

Commonwealth Scientific and Industrial Research Organisation (CSIRO) Environment presented a summary of over 40years of atmospheric $CO_2$ stable isotope measurements with comprehensive information on the use of RMs, reporting scales, international comparisons, and measurement uncertainties.

The session was concluded with an overview of the recommendations from the Workshop on Carbon Dioxide and Methane Stable Isotope Ratio Measurements, organized by a new task group under the aegis of CCQM gas analysis working group (GAWG) and isotope ratio working group (IRWG) [67].

## 6.2 | Organic and Inorganic RMs

IAEA is producing and characterizing two wood RMs (one from a C3 plant and one from a C4 plant, both characterized for $\delta(^{13}C)$, $\delta(^{18}O)$, and $\delta(^{2}H)$) and three gaseous $CO_2$ RMs ($\delta(^{13}C)$ and $\delta(^{18}O)$). Moreover, IAEA is releasing the second batch of IAEA-CH-6 (characterized for $\delta(^{13}C)$) and, in collaboration with USGS and McMaster University, is reprocessing and reassessing IAEA-CO-8 carbonatite (characterized for $\delta(^{13}C)$ and $\delta(^{18}O)$).

Six organic RMs of different natural matrices (all characterized for $\delta(^{13}C)$, $\delta(^{15}N)$, and $\delta(^{34}S)$) are under processing and characterization, within the context of a collaboration among NIST, IAEA, and GNS Science (New Zealand).

USGS is finalizing the characterization of USGS19 and USGS20 as new calcite reference materials for $\delta(^{13}C)$ and $\delta(^{18}O)$ measurements.

## 6.3 | Value Assignment and Uncertainty Assessment of RMs

According to ISO 17034:2016 [7], the characterization of RMs can be based on interlaboratory comparison involving measurements by expert laboratories. Most expert laboratories contributing to characterizing new isotope delta RMs are not accredited. It was agreed that accreditation itself is desirable but not essential; rather, a reliable system through which expert laboratories can demonstrate their expertise is required. Drafting guidelines on how competency for expert laboratories can be demonstrated was suggested.

Basic uncertainty propagation principles for stable isotope values assignment to RMs and reassessment of RMs on the VPDB-LSVEC scale were presented [34]. Online statistical modelling tools to recognize the finer structure of data and to assign value and uncertainty to RM have been provided by NIST (consensus.nist.gov and decisiontree.nist.gov) and NRC (metrology.shinyapps.io/consensus-calculator/). A paper, “Interlaboratory comparisons of chemical measurements: Quo Vadis?” on this topic, was recently published in *Accreditation and Quality Assurance* [68].

It was recommended to centralize the storage of the data used for RM characterization (raw data, RMs with reference values, and other relevant information) to facilitate data evaluation and re-evaluation. Moreover, the need to develop guidelines for data processing to avoid underestimation of uncertainty was recognized.

## 6.4 | $\delta(^{2}H)$ of Non-exchangeable Hydrogen in Organic Materials

The non-exchangeable hydrogen, also known as intrinsic hydrogen, is typically a C-H bonded material of interest that retains the environmental signal upon formation (e.g., for paleoclimate reconstruction). Exchangeable hydrogen in organic matter refers to hydrogen ions that are loosely bound and can be readily exchanged in the surrounding environment, typically ambient water vapor. In organic matter, hydrogen ions are often associated with functional groups such as carboxyl (-COOH), phenolic (-OH), and amino ($-NH_2$) groups. The fraction of exchangeable hydrogen varies by material and can be low (<2%–3% for wood) to high (22% for glycine). The $\delta(^{2}H)$ determination of the non-exchangeable hydrogen in bulk organic materials requires both operational methods to remove or control the exchangeable fraction and the assumption of a hydrogen isotope fractionation factor. Various operational approaches in the literature over the past decades do not give consistent $\delta(^{2}H)$ results with acceptable uncertainty and can vary by 10‰–80‰ among laboratories. Accordingly, for all available organic RMs with exchangeable hydrogen, the $\delta(^{2}H)$ determination of the non-exchangeable hydrogen values must remain provisional. Efforts are underway to standardize approaches for estimating the non-exchangeable hydrogen isotopic compositions of current organic RMs [69].

## 6.5 | Carbonate Phosphoric Acid Reaction

MPI-BGC presented the state of the art in $CO_2$ evolution from solid carbonates, but a standard operating procedure (SOP) has not yet been developed. Work towards an agreed uncertainty budget and demonstrated consistency between laboratories using the phosphoric acid/carbonate reference system, especially for $\delta(^{18}O)$ measurements, is encouraged.

## 6.6 | Calculation of $\delta(^{13}C)$ and $\delta(^{18}O)$ of $CO_2$ Measured by DI-IRMS

A guide on applying the corrections and other calculations to obtain the $\delta(^{13}C)$ and $\delta(^{18}O)$ values and uncertainties of $CO_2$ measured by DI-IRMS is under draft. A calculation spreadsheet with a simple recipe and explanation has been developed, which once validated and approved by experts, can be used by the users to reach minimum requirements for quality data.

## 7 | Conclusion

The panel of experts at the IAEA meeting (Vienna, 22–26 January, 2024) recommended consistent reporting of isotope delta values for hydrogen, carbon, nitrogen, oxygen, and sulfur, according to IUPAC guidelines and commonly agreed definitions and realizations of the delta scales. Two stable carbon isotope delta scales were acknowledged and defined as VPDB and VPDB-LSVEC. For oxygen, the VSMOW-SLAP scale was defined and recognized as the primary oxygen isotope delta scale and the VPDB or VPDB-$CO_2$ scale has been defined in terms of the VSMOW-SLAP scale.

It is crucial for users to specify the RMs used to normalize data, the values of these RMs, and which scale was used for normalization. RM producers should be clear about the traceability of any carbon isotope delta values assigned to materials they produce or distribute so that users can make informed choices. When the traceability is unclear or the specific scale is not mentioned, users should consider the bias between results reported on the different carbon isotope scales. Uncertainties of RMs must be considered in the assessment of measurement uncertainty, and, for RMs on VPDB-LSVEC scale, an additional component of uncertainty may be required. Embracing these recommendations will enhance transparency, reliability, and reproducibility in the reporting of stable isotope results and will thereby minimize hidden biases.

It was agreed to conduct additional research aimed at enhancing the consistency across various laboratories of isotopic analysis of "non-exchangeable hydrogen" in bulk organic materials and of oxygen in carbonates through the phosphoric acid reaction. The development of new RMs especially for greenhouse gases and of harmonized protocols for data calculation and normalization and for assigning value and uncertainty to RMs was also recommended.

### Author Contributions

**Federica Camin:** conceptualization, investigation, writing – original draft, writing – review and editing. **Dinka Besic:** writing – review and editing. **Paul J. Brewer:** writing – original draft, writing – review and editing. **Colin E. Allison:** investigation, writing – review and editing. **Tyler B. Coplen:** investigation, writing – review and editing. **Philip J.H. Dunn:** investigation, writing – original draft, writing – review and editing. **Matthias Gehre:** writing – review and editing. **Manfred. Gröning:** writing – review and editing. **Harro A.J. Meijer:** investigation, writing – original draft, writing – review and editing. **Jean-François Hélie:** investigation, writing – review and editing. **Paola Iacumin:** writing – review and editing. **Rebecca Kraft:** writing – review and editing. **Bor Krajnc:** investigation, writing – review and editing. **Steffen Kümmel:** writing – review and editing. **Sangil Lee:** writing – review and editing. **Juris Meija:** investigation, writing – original draft, writing – review and editing. **Zoltan Mester:** investigation, writing – review and editing. **Joachim Mohn:** writing – review and editing. **Heiko Moossen:** writing – review and editing, investigation. **Haiping Qi:** investigation, writing – review and editing. **Grzegorz Skrzypek:** investigation, writing – review and editing. **Peter Sperlich:** writing – review and editing. **Joelle Viallon:** writing – review and editing. **Leonard I. Wassenaar:** writing – review and editing, writing – original draft. **Robert I. Wielgosz:** investigation, writing – original draft, writing – review and editing.

### Acknowledgments

The authors would like to thank Arndt Schimmelmann of Indiana University, the three anonymous reviewers and the editor Roland Bol who have substantially enhanced the readability of the manuscript with their comments and suggestions.

### Data Availability Statement

Data sharing not applicable to this article as no datasets were generated or analysed during the current study.

### Peer Review

The peer review history for this article is available at https://www.webofscience.com/api/gateway/wos/peer-review/10.1002/rcm.10018.

### References

1. S. Assonov, "Summary and Recommendations From the International Atomic Energy Agency Technical Meeting on the Development of Stable Isotope Reference Products (21–25 November 2016)," *Rapid Communications in Mass Spectrometry* 32 (2018): 827–830, https://doi.org/10.1002/rcm.8102.

2. R. Gonfiantini, "*Stable* Isotope Standards *and Intercalibration in Hydrology and in Geochemistry (Rep. Consultants Group Meeting, Vienna, 1976)*," International Atomic Energy Agency, (1977): 1–29.

3. B. E. Taylor, T. Ding, S. Halas, O. Breas, and B. W. Robinson, "Accurate Calibration of the V-CDT Scale: Proposed $\delta^{34}S$ Values for Calibration Materials and Methods of Correction for $SO_2$-Based Analyses," International Atomic Energy Agency (2000): 7.

4. IAEA, "Reference and Intercomparison Materials for Stable Isotopes of Light Elements," International Atomic Energy Agency, (1995):1–168. accessed August 22, 2024, https://www.iaea.org/publications/5471/reference-and-intercomparison-materials-for-stable-isotopes-of-light-elements.

5. R. Gonfiantini, "*Stable Isotope Reference Samples for Geochemical and Hydrochemical Investigations (Rep. Advisory Group Meeting, Vienna, 1983)*," International Atomic Energy Agency, (1984): 1–77.

6. G. Skrzypek, C. E. Allison, J. K. Böhlke, et al., "Minimum Requirements for Publishing Hydrogen, Carbon, Nitrogen, Oxygen and Sulfur Stable-Isotope Delta Results (IUPAC Technical Report)," *Pure and Applied Chemistry* 94, no. 11–12 (2022): 1249–1255, https://doi.org/10.1515/pac-2021-1108.

7. ISO, "General Requirements for the Competence of Reference Material Producers (ISO 17034:2016)," International Organization for Standardization, (2016):1–24.

8. "Decision CIPM/104–26, Traceability Exception: Delta Value Isotope Ratio Measurements," CIPM (2015), https://www.bipm.org/documents/20126/48101963/Traceability-Exception-QM1.pdf/ca63c530-c553-60a1-9111-406c66de4c4d.

9. W. A. Brand, T. B. Coplen, J. Vogl, M. Rosner, and T. Prohaska, "Assessment of International Reference Materials for Isotope-Ratio Analysis (IUPAC Technical Report)," *Pure and Applied Chemistry* 86 (2014): 425–467, https://doi.org/10.1515/pac-2013-1023.

10. BIPM, "The International System of Units (SI) 9th edn Version 3.01," (2024), www.bipm.org/en/publications/si-brochure.

11. P. J. Dunn, D. Malinovsky, N. Ogrinc, et al., "Re-Determination of R ($^{13}C/^{12}C$) for Vienna Peedee Belemnite (VPDB)," *Rapid Communications*

*in Mass Spectrometry* 38, no. 16 (2024): e9773, https://doi.org/10.1002/rcm.9773.

12. I. Friedmann, J. O'Neil, and G. Cebula, "Two New Carbonate Stable-Isotope Standards," *Geostandards Newsletter* 6 (1982): 11–12, https://doi.org/10.1111/j.1751-908X.1982.tb00340.x.

13. G. Hut, "*Stable Isotope Reference Samples for Geochemical and Hydrological Investigations (Rep. Consultants Group Meeting, Vienna, 1985)*," International Atomic Energy Agency, (1987): 1–42.

14. T. B. Coplen, "Guidelines and Recommended Terms for Expression of Stable-Isotope-Ratio and gas-Ratio Measurement Results," *Rapid Communications in Mass Spectrometry* 25, no. 17 (2011): 2538–2560, https://doi.org/10.1002/rcm.5129.

15. A. M. Van Der Veen, J. Meija, A. Possolo, and D. B. Hibbert, "Interpretation and use of Standard Atomic Weights (IUPAC Technical Report)," *Pure and Applied Chemistry* 93, no. 5 (2021): 629–646, https://doi.org/10.1515/pac-2017-1002.

16. T. B. Coplen, W. A. Brand, M. Gehre, et al., "New Guidelines for $\delta^{13}$C Measurements," *Analytical Chemistry* 78 (2006): 2439–2441, https://doi.org/10.1021/ac052027c.

17. T. B. Coplen, W. A. Brand, M. Gehre, et al., "After Two Decades a Second Anchor for the VPDB $\delta^{13}$C Scale," *Rapid Communications in Mass Spectrometry* 20 (2006): 3165–3166, https://doi.org/10.1002/rcm.2727.

18. H. P. Qi, T. B. Coplen, S. J. Mroczkowski, et al., "A New Organic Reference Material, L-Glutamic Acid, USGS41a, for $\delta^{13}$C and $\delta^{15}$N Measurements - A Replacement for USGS41," *Rapid Communications in Mass Spectrometry* 30 (2016): 859–866, https://doi.org/10.1002/rcm.7510.

19. CIAAW, "Standard Atomic Weights of 14 Chemical Elements Revised," *Chemistry International* 40, no. 4 (2018): 23–24, https://doi.org/10.1515/ci-2018-0409.

20. IAEA, "Reference Sheet, Reference Material LSVEC (Li-Carbonate), Reference Material for Li-Isotope Ratio," (2020), Last Accessed: 5th December 2022, https://nucleus.iaea.org/sites/referencematerials/pages/lsvec.aspx.

21. P. J. Dunn and F. Camin, "The 'LSVEC Problem'for the Vienna Peedee Belemnite Carbon Isotope-Delta Scale," *Rapid Communications in Mass Spectrometry* 38, no. 17 (2024): 1–1606, https://doi.org/10.1002/rcm.9841.

22. J. F. Hélie, A. Adamowicz-Walczak, P. Middlestead, M. M. G. Chartrand, Z. Mester, and J. Meija, "Discontinuity in the Realization of the Vienna Peedee Belemnite Carbon Isotope Ratio Scale," *Analytical Chemistry* 93, no. 31 (2021): 10740–10743, https://doi.org/10.1021/acs.analchem.1c02458.

23. S. Assonov, A. Fajgelj, J. F. Hélie, C. Allison, and M. Gröning, "Characterisation of New Reference Materials IAEA-610, IAEA-611 and IAEA-612 Aimed at the VPDB $\delta^{13}$C Scale Realisation With Small Uncertainty," *Rapid Communications in Mass Spectrometry* 35 (2021): e9014, https://doi.org/10.1002/rcm.9014.

24. H. P. Qi, H. Moossen, H. A. J. Meijer, et al., "USGS44, a New High-Purity Calcium Carbonate Reference Material for $\delta^{13}$C Measurements," *Rapid Communications in Mass Spectrometry* 35, no. 4 (2021): 17, https://doi.org/10.1002/rcm.9006.

25. "CIAAW 20 December 2024 News," accessed January 6, 2025, https://ciaaw.org/news.htm.

26. W. A. Brand, S. Assonov, and T. B. Coplen, "Correction for the $^{17}$O Interference in $\delta(^{13}$C) Measurements When Analyzing $CO_2$ With Stable Isotope Mass Spectrometry (IUPAC Technical Report)," *Pure and Applied Chemistry* 82, no. 8 (2010): 1719–1733, https://doi.org/10.1351/PAC-REP-09-01-05.

27. S. Assonov, M. Gröning, A. Fajgelj, J. F. Hélie, and C. Hillaire-Marcel, "Preparation and Characterisation of IAEA-603, a New Primary Reference Material Aimed at the VPDB Scale Realisation for $\delta^{13}$C and $\delta^{18}$O Determination," *Rapid Communications in Mass Spectrometry* 34, no. 20 (2020): e8867, https://doi.org/10.1002/rcm.8867.

28. T. Prohaska, J. Irrgeher, J. Benefield, et al., "Standard Atomic Weights of the Elements 2021 (IUPAC Technical Report)," *Pure and Applied Chemistry* 94, no. 5 (2022): 573–600, https://doi.org/10.1515/pac-2019-0603.

29. G. D. Flesch, A. R. Anderson, Jr., and H. J. Svec, "A Secondary Isotopic Standard for $^{6}$Li/$^{7}$Li Determinations," *International Journal of Mass Spectrometry and Ion Physics* 12 (1973): 265–272, https://doi.org/10.1016/0020-7381(73)80043-9.

30. "Reference Material 8545 LSVEC, 24 January, 2023," accessed September 2, 2024, https://tsapps.nist.gov/srmext/certificates/8545.pdf.

31. A. Schimmelmann, H. Qi, T. B. Coplen, et al., "Organic Reference Materials for Hydrogen, Carbon, and Nitrogen Stable Isotope-Ratio Measurements: Caffeines, n-Alkanes, Fatty Acid Methyl Esters, Glycines, L-Valines, Polyethylenes, and Oils," *Analytical Chemistry* 88 (2016): 4294–4302, https://doi.org/10.1021/acs.analchem.5b04392.

32. A. Schimmelmann, H. Qi, P. J. H. Dunn, et al., "Food Matrix Reference Materials for Hydrogen, Carbon, Nitrogen, Oxygen, and Sulfur Stable Isotope-Ratio Measurements: Collagens, Flours, Honeys, and Vegetable Oils," *Journal of Agricultural and Food Chemistry* 68, no. 39 (2020): 10852–10864, https://doi.org/10.1021/acs.jafc.0c02610.

33. M. M. G. Chartrand, J. Meija, P. Kumkrong, and Z. Mester, "Three Certified Sugar Reference Materials for Carbon Isotope Delta Measurements," *Rapid Communications in Mass Spectrometry* 33 (2019): 272–280, https://doi.org/10.1002/rcm.8357.

34. M. Gröning, "Some Pitfalls in the Uncertainty Evaluation of Isotope Delta Reference Materials," *Accreditation and Quality Assurance* 28, no. 3 (2023): 101–114, https://doi.org/10.1007/s00769-022-01527-6.

35. M. M. Chartrand, F. H. Liu, J. P. Merrick, et al., "Final Report for CCQM-P212: Coherence of Carbon Isotope Delta Reference Materials," *Metrologia* 60, no. 1A (2023): 08028, https://doi.org/10.1088/0026-1394/60/1A/08028.

36. S. Assonov, "Perspective: On the Discontinuity Between the Scale Realizations VPDB2020 and VPDB2006–The Underestimated Role of Measurement Uncertainties?," *Rapid Communications in Mass Spectrometry* 38, no. 15 (2024): e9779, https://doi.org/10.1002/rcm.9779.

37. JCGM, "Guides to the Expression of Uncertainty in Measurement (GUM), Joint Committee for Guides in Metrology (JCGM), JCGM GUM-1:2023 1st Edition," Last Accessed: 5th December 2024, https://doi.org/10.59161/JCGMGUM-1–2023.

38. H. Qi and T. B. Coplen, "Report of Stable Isotopic Composition Reference Material USGS44," accessed February 11, 2025, https://www.usgs.gov/media/files/rsil-report-stable-isotopic-composition-reference-material-usgs44-0.

39. T. B. Coplen, "Reporting of Stable Hydrogen, Carbon and Oxygen Isotopic Abundances," *Pure and Applied Chemistry* 66 (1994): 273–276, https://doi.org/10.1351/pac199466020273.

40. T. B. Coplen, C. Kendall, and J. Hopple, "Comparison of Stable Isotope Reference Samples," *Nature* 302 (1983): 236–238, https://doi.org/10.1038/302236a0.

41. R. M. Verkouteren and D. B. Klinedinst, "Value Assignment and Uncertainty Estimation of Selected Light Stable Isotope Reference Materials: RMs 8543–8545, RMs 8562–8564, and RM 8566," National Institute of Standards and Technology, (2004):1–56.

42. H. A. Meijer, "Stable Isotope Quality Assurance Using the 'Calibrated IRMS'strategy," *Isotopes in Environmental and Health Studies* 45, no. 2 (2009): 150–163, https://doi.org/10.1080/10256010902869113.

43. C. Hillaire-Marcel, S. T. Kim, A. Landais, et al., "A Stable Isotope Toolbox for Water and Inorganic Carbon Cycle Studies," *Nature Reviews Earth and Environment* 2 (2021): 699–719, https://doi.org/10.1038/s43017-021-00209-0.

44. P. Baertschi, “Absolute $^{18}$O Content of Standard Mean Ocean Water,” *Earth and Planetary Science Letters* 31 (1976): 341–344, https://doi.org/10.1016/0012-821X(76)90115-1.

45. W. Li, B. Ni, D. Jin, and Q. Zhang, “Measurement of the Absolute Abundance of Oxygen-17 in V-SMOW,” *KEXUE TONGBAO Chin Sci Bull.* 33 (1988): 1610–1613.

46. S. Epstein and T. Mayeda, “Variation of $^{18}$O Content of Waters From Natural Sources,” *Geochimica et Cosmochimica Acta* 4 (1953): 213–224, https://doi.org/10.1016/0016-7037(53)90051-9.

47. I. Friedman and J. R. O'Neill, “Compilation of Stable Isotope Fractionation Factors of Geochemical Interest,” U.S. Geolog. Survey, (1977).

48. W. G. Mook, “Volume I: Introduction: Theory, Methods, Review,” Vol 1. International Hydrological Programme IHP-V, UNESCO, IAEA, (2000).

49. R. Gonfiantini, “Standards for Stable Isotope Measurements in Natural Compounds,” *Nature* 271 (1978): 534–536.

50. A. T. Aerts-Bijma, A. C. van Buuren, D. Paul, and H. A. Meijer, “The Absolute $\delta^{18}$O Value for SLAP With Respect to VSMOW Reveals a Much Lower Value Than Previously Established,” *Rapid Communications in Mass Spectrometry* 38, no. 6 (2024): e9678, https://doi.org/10.1002/rcm.9678.

51. S. T. Kim, T. B. Coplen, and J. Horita, “Normalization of Stable Isotope Data for Carbonate Minerals: Implementation of IUPAC Guidelines,” *Geochimica et Cosmochimica Acta* 158 (2015): 276–289, https://doi.org/10.1016/j.gca.2015.02.011.

52. P. Iacumin, M. Rossi, and G. Venturelli, “Oxygen Isotope Phosphoric Acid Fractionation Factor and Uncertainty on the $\delta^{18}$O Measurements of Calcite,” *Applied Sciences* 12, no. 19 (2022): 10094, https://doi.org/10.3390/app121910094.

53. A. Mariotti, “Atmospheric Nitrogen Is a Reliable Standard for Natural $^{15}$N Abundance Measurements,” *Nature* 303 (1983): 685–687, https://doi.org/10.1038/303685a0.

54. J. K. Böhlke and T. B. Coplen, *Interlaboratory Comparison of Reference Materials for Nitrogen-Isotope-Ratio Measurements* (Vienna: International Atomic Energy Agency, 1995): 67–74.

55. H. P. Qi, T. B. Coplen, H. Geilmann, W. A. Brand, and J. K. Böhlke, “Two New Organic Reference Materials for $\delta^{13}$C and $\delta^{15}$N Measurements and a New Value for the $\delta^{13}$C of NBS 22 Oil,” *Rapid Communications in Mass Spectrometry* 17 (2003): 2483–2487, https://doi.org/10.1002/rcm.1219.

56. H. R. Krouse and T. B. Coplen, “Reporting of Relative Sulfur Isotope-Ratio Data,” *Pure and Applied Chemistry* 69, no. 2 (1997): 293–295, https://doi.org/10.1351/pac199769020293.

57. P. Sperlich, H. Moossen, H. Geilmann, et al., “A Robust Method for Direct Calibration of Isotope Ratios in Gases Against Liquid/Solid Reference Materials, Including a Laboratory Comparison for $\delta^{13}$C-$CH_4$,” *Rapid Communications in Mass Spectrometry* 35, no. 1 (2021): 6, https://doi.org/10.1002/rcm.8944.

58. P. Sperlich, N. A. M. Uitslag, J. M. Richter, et al., “Development and Evaluation of a Suite of Isotope Reference Gases for Methane in Air,” *Atmospheric Measurement Techniques* 9 (2016): 3717–3737, https://doi.org/10.5194/amt-9-3717-2016.

59. P. Sperlich, F. Camin, K. Deufrains, et al., “Measurement of the Stable Carbon Isotope Ratio in Atmospheric CH4 Using Laser Spectroscopy for $CH_4$ Source Characterization,” International Atomic Energy Agency, (2024), https://www.iaea.org/publications/15734/measurement-of-the-stable-carbon-isotope-ratio-in-atmospheric-ch4-using-laser-spectroscopy-for-ch4-source-characterization.

60. P. J. Brewer, J. S. Kim, S. Lee, et al., “Advances in Reference Materials and Measurement Techniques for Greenhouse Gas Atmospheric Observations,” *Metrologia* 56, no. 3 (2019): 034006, https://doi.org/10.1088/1681-7575/ab1506.

61. J. Viallon, T. Choteau, E. Flores, et al., “Final Report of CCQM-P204, Comparison on $CO_2$ Isotope Ratios in Pure CO2,” *Metrologia* 60, no. 1A (2023): 08026, https://doi.org/10.1088/0026-1394/60/1A/08026.

62. J. Y. Lee, K. Marti, J. P. Severinghaus, et al., “A Redetermination of the Isotopic Abundances of Atmospheric Ar,” *Geochimica et Cosmochimica Acta* 70 (2006): 4507–4512, https://doi.org/10.1016/j.gca.2006.06.1563.

63. D. Min, J. B. Lee, C. Lee, D. S. Lee, and J. S. Kim, “Estimation of Mass Discrimination Factor for a Wide Range of m/z by Argon Artificial Isotope Mixtures and $NF_3$ gas,” *Bulletin of the Korean Chemical Society* 35, no. 8 (2014): 2403–2409, https://doi.org/10.5012/bkcs.2014.35.8.2403.

64. N. E. Ostrom, H. Gandhi, T. B. Coplen, et al., “Preliminary Assessment of Stable Nitrogen and Oxygen Isotopic Composition of USGS51 and USGS52 Nitrous Oxide Reference Gases and Perspectives on Calibration Needs,” *Rapid Communications in Mass Spectrometry* 32 (2018): 1207–1214, https://doi.org/10.1002/rcm.8157.

65. N. E. Ostrom, H. Gandhi, T. B. Coplen, et al., “Preliminary Assessment of Stable Nitrogen and Oxygen Isotopic Composition of USGS51 and USGS52 Nitrous Oxide Reference Gases and Perspectives on Calibration Needs,” *Rapid Communications in Mass Spectrometry* 32, no. 20 (2018): 1829–1830, https://doi.org/10.1002/rcm.8257.

66. J. Mohn, C. Biasi, S. Bodé, et al., “Isotopically Characterised $N_2O$ Reference Materials for Use as Community Standards,” *Rapid Communications in Mass Spectrometry* 36, no. 13 (2022): e9296, https://doi.org/10.1002/rcm.9296.

67. “CCQM GAWG-IRWG Workshop on Carbon Dioxide and Methane Stable Isotope Ratio Measurements, Recommendations, Laboratorio Tecnológico del Uruguay (LATU), Montevideo, Uruguay, 9–10 October 2023,” accessed September 2, 2024, https://www.bipm.org/documents/20126/215802027/Isotope+Ratio+Workshop+Report/5c5f0393-e5f4-1bba-7e40-db6fd9b18a89.

68. J. Meija and A. Possolo, “Interlaboratory Comparisons of Chemical Measurements: Quo Vadis?,” *Accreditation and Quality Assurance* 28, no. 3 (2023): 89–93, https://doi.org/10.1007/s00769-022-01505-y.

69. L. I. Wassenaar, L. Sisti, M. Pilecky, and M. Kainz, “Reproducible Measurements of the $\delta^{2}$H Composition of Non-Exchangeable Hydrogen in Complex Organic Materials Using the UniPrep2 Online Static Vapour Equilibration and Sample Drying System,” *MethodsX.* 10 (2023): 101984, https://doi.org/10.1016/j.mex.2022.101984.