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PERSPECTIVE

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The 'LSVEC problem' for the Vienna Peedee belemnite carbon isotope-delta scale

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Since 2016 there have been intense discussions within several established communities and networks regarding the consequences of the withdrawal of the LSVEC lithium carbonate reference material for carbon isotope-delta measurement calibration. These include the Isotope Ratio Working Group (IRWG) of the Consultative Committee for the Amount of Substance (CCQM, French: Comité Consultatif pour la Quantité de Matière) of the International Committee of Weights and Measures (CIPM, French: Comité International des Poids et Mesures); participants within the 2016, 2021 and 2024 Technical Meetings on International Atomic Energy Agency (IAEA) stable isotope ratio reference products; and the International Union of Pure and Applied Chemistry's Commission on Isotopic Abundances and Atomic Weights (IUPAC CIAAW) amongst others. The reasons for these intensive discussions relate to the privileged position that LSVEC has occupied for traceability of carbon isotope-delta measurements relative to Vienna Peedee belemnite (VPDB) and the potential implications of its withdrawal for all current and future measurements of carbon isotope-delta values. This perspective summarises the background information regarding the LSVEC material in the context of the VPDB carbon isotope-delta scale. The various proposals to address the LSVEC problem that have been discussed within those committees and networks are also presented. The information herein was used as a foundation for discussions at the 2024 IAEA Consultancy Meetings on the Development of IAEA Stable Isotope Reference Materials and Related Products and on the Definition and Realisation of the Isotopic Delta Scales for Light Elements (22–26 January 2024, Vienna, Austria). A summary of those 2024 meetings and associated outcomes can be found elsewhere.

1 | CARBON ISOTOPE DELTA AND THE VPDB SCALE

Carbon isotope-delta values are relative differences in carbon isotope ratio between a sample and a reference.[1, 2] By definition, the carbon isotope delta of the reference relative to itself is exactly zero as the isotope ratios of the sample and reference are exactly equal to one another (isotope delta references are sometimes referred to as 'zero points'). While this is correct in theory, in practice it is important to note that taking two aliquots of the same reference and measuring

the isotope delta between them will not yield zero with no uncertainty as the material may not be completely homogeneous and any measurement has some associated measurement uncertainty. There is therefore a small distinction between theory and practical measurements.

The original reference used amongst laboratories performing stable carbon isotope ratio measurements was Peedee belemnite (PDB). This was described as '*carbon dioxide prepared from a Cretaceous belemnite*, Belemnitella americana, *from the Peedee formation of South Carolina*'.[1,3,4] As noted above, by definition, the carbon isotope-delta value of PDB relative to itself must be exactly zero; however, the PDB carbonate material was likely heterogeneous (see Table VI of Gonfiantini[5]).

In 1987, it was recommended by IAEA consultants that the VPDB carbon isotope-delta scale be internationally adopted to make it clear that carbon isotope-delta values were no longer being expressed relative to PDB that existed in some laboratories.[6] The zero point of the scale, VPDB itself, was defined by assigning an exact carbon isotope-delta value to the calcium carbonate reference material (RM) NBS 19 of $\delta_{VPDB}(^{13}C/^{12}C) = +1.95‰$. In this way, NBS 19 became the primary RM for VPDB, which itself did not exist in material form. Its non-zero assigned value was the result of an interlaboratory comparison for NBS 19 relative to the original PDB material (see Table VI of Gonfiantini[5]). This ensured that carbon isotope-delta values traceable to the new VPDB defined by NBS 19 would have the smallest possible bias when compared to carbon isotope-delta values traceable to the original PDB. As a result, some consider that this VPDB scale is not completely separate from the original PDB scale.

From this definition of VPDB it is apparent that NBS 19 has two roles: it is both a material with an exactly assigned isotope delta value on the VPDB scale and a RM that can be used in practical measurements to calibrate results to the VPDB scale. To clarify the difference between these roles a schematic representation of an isotope-delta scale is useful. One might represent the relationship between the PDB and VPDB scales according to Figure 1. Within Figure 1, solid lines represent the scales, while the defined points on the scales are shown as filled circles (all defined points on scales have zero uncertainty as they are assigned by convention, for example by selection of the isotope-delta reference or zero point). Defined points that are virtual materials such as VPDB have no fill. RMs that realise points on the scales in practice are shown above the scales; those with exact isotope-delta values which define the scale (the primary RMs) are shown as circles. RMs with non-zero associated uncertainty are ovals and the wider the oval, the larger the uncertainty. Dashed lines represent the traceability of RMs to the primary RM. The PDB and VPDB scales are aligned at the isotope-delta value of NBS 19.

Hopefully with Figure 1 it is now a little clearer that some materials such as VPDB are defined points on a scale but are of no practical use as there is no equivalent material that can be purchased and used as a RM for calibration. Other materials such as PDB and NBS 19 are both exactly defined points on a scale, but are (or in the case of PDB, were) also available for direct use during calibration of measurement results. Note that those extant materials, particularly the original PDB, may not be completely homogeneous even though they have isotope-delta values that have an associated uncertainty that is zero by definition.[5]

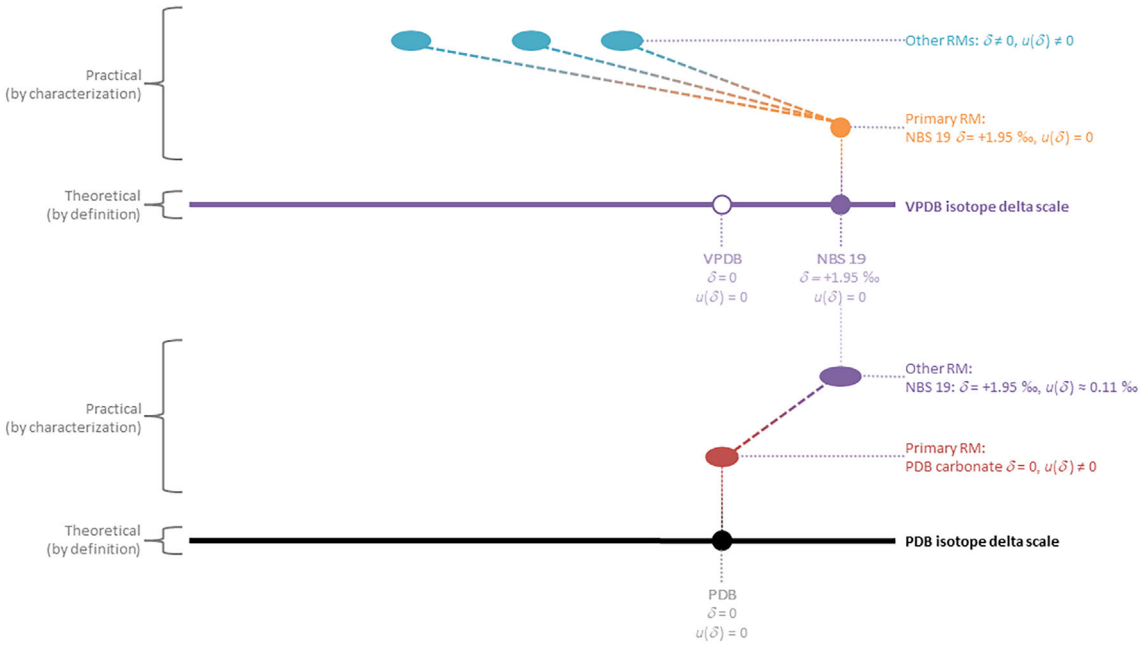

FIGURE 1 Schematic representation of the PDB carbon isotope-delta scale (black line) together with the VPDB scale as defined by Hut[6] (purple line). Neither are to scale. Note that the uncertainty associated with NBS 19 on the PDB scale is likely predominately due to heterogeneity of the PDB carbonate [Color figure can be viewed at wileyonlinelibrary.com]

2 | INTRODUCTION OF LSVEC AS AN ADDITIONAL PRIMARY RM FOR VPDB

In 2006, an inter-laboratory recalibration of RMs for carbon isotope-delta traceable to VPDB found that adopting a second RM for normalisation significantly reduced inter-laboratory variance. It was then recommended that all carbon isotope-delta values relative to VPDB be normalised such that the LSVEC lithium carbonate material would have $\delta_{VPDB}(^{13}C/^{12}C) = -46.6‰$, exactly.[7,8] This was similar to the decades-old recommendation that hydrogen and oxygen isotope-delta measurements relative to Vienna Standard Mean Ocean Water (VSMOW) be normalised to exact isotope-delta values assigned to Standard Light Antarctic Precipitation (SLAP).[6,9,10] As a result, the majority of carbon isotope-delta RMs available since 2006 have traceability chains that include both NBS 19 and LSVEC, each with exactly assigned carbon isotope-delta value.[11,12]

The scale modified in 2006 can be represented by Figure 2 and is commonly referred to as VPDB-LSVEC to distinguish it from the original VPDB.

The assigned carbon isotope-delta value for LSVEC was derived from various measurement results.[8] These included the Ghosh et al[13] value of $\delta_{VPDB}(^{13}C/^{12}C) = -46.607‰$ from the measurement of three batches containing a total of nine flasks of carbon dioxide prepared from the LSVEC carbonate by phosphoric acid digestion. The within-batch standard deviation was reported to be 0.029‰ and the between-batch standard deviation 0.018‰.[13] A combined uncertainty for this measurement result of 0.057‰ has also been reported.[8] The measurement result for the carbon isotope delta of LSVEC from Verkouteren and Klinedinst[14] was also considered during the assignment of the exact carbon isotope-delta value for LSVEC. They reported a value of $\delta_{VPDB}(^{13}C/^{12}C) = -46.57 \pm 0.12‰$ for LSVEC taken as the mean and between-laboratory standard deviation using the results from seven different laboratories (two of the seven results were excluded from the calculation for not meeting performance requirements).[14]

Un-normalised carbon isotope-delta values for LSVEC were also reported by participants in the 2006 re-evaluation of between $\delta_{VPDB}(^{13}C/^{12}C) = -46.015‰$ and $\delta_{VPDB}(^{13}C/^{12}C) = -46.496‰$.[8] Older measurement results for LSVEC carbon isotope delta relative to VPDB include the Qi et al[15] value of $\delta_{VPDB}(^{13}C/^{12}C) = -46.46 \pm 0.12‰$ (mean and standard deviation of the five reported results from two different laboratories) and the value reported by Stichler[16] within IAEA TECDOC 825 of $\delta_{VPDB}(^{13}C/^{12}C) = -46.479 = 0.150‰$. A summary of the various reported LSVEC carbon isotope-delta values relative to VPDB can be found in Figure 3. The majority are less negative than the assigned value of $\delta_{VPDB}(^{13}C/^{12}C) = -46.6‰$.

The introduction of LSVEC as an additional primary RM was not considered at the time to introduce a new carbon isotope-delta scale, but simply provide a means to reduce inter-laboratory variance with a new calibration protocol. Carbon isotope-delta values for RMs traceable to NBS 19 alone should coincide with those traceable to both NBS 19 and LSVEC within uncertainty, but the uncertainty associated to values traceable to VPDB-LSVEC would be lower. Using the VPDB-LSVEC name would simply distinguish results traceable to both NBS 19 and LSVEC from those traceable to only NBS 19.

For RMs with less negative $\delta_{VPDB}(^{13}C/^{12}C)$ values such as IAEA-CO-8 and NBS 18, the introduction of LSVEC into the traceability chain did not change significantly their assigned values as the changes were lower than their previously assigned uncertainty. For other RMs, such as the NIST CO_2 RMs (SRM 8562, 8563 and 8564) and IRMM BCR-656 ethanol and BCR-657 glucose, only the results of single-point calibrations to NBS 19 alone were available and therefore they did not have a change in the traceability chain for their assigned carbon isotope-delta values and were therefore still traceable to the VPDB as defined by Hut.[6] It was only for RMs with more negative $\delta_{VPDB}(^{13}C/^{12}C)$ values such as NBS 22 mineral oil that changes to assigned carbon isotope-delta values were significant, but this was in part due to better agreement between laboratories resulting from the use of two-point calibration.

For analysts, the introduction of LSVEC simply required that two (or more) RMs be used for calibration of measurement results and the use of the newly assigned values and uncertainties for some RMs. Changes in RM assigned values and/or uncertainties can also occur when the RM producer performs additional measurements, re-evaluates existing data or uncovers additional components to uncertainty such as a contribution from long-term stability and are therefore not wholly unfamiliar.

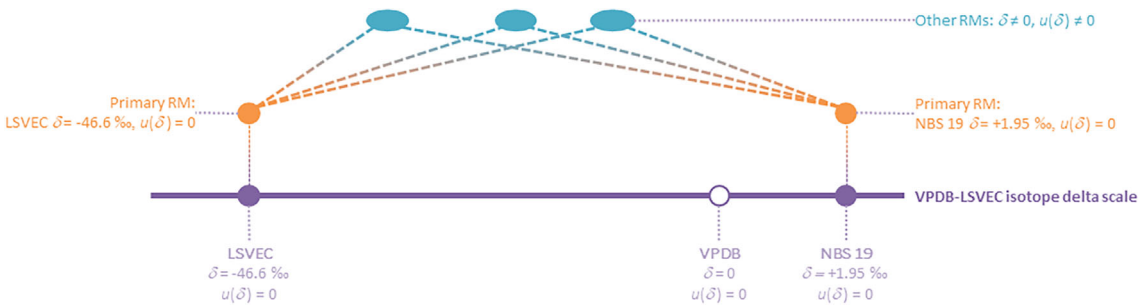

FIGURE 2 Schematic representation of the VPDB-LSVEC carbon isotope-delta scale following the introduction of LSVEC as an additional primary RM in 2006 (not to scale). The original PDB scale is not shown [Color figure can be viewed at wileyonlinelibrary.com]

3 | THE 'LSVEC PROBLEM'

Approximately a decade after its introduction as an additional primary RM, the IAEA found significant deviations in carbon isotope delta between vials of LSVEC. These were found in both opened and unopened vials as well as within bulk containers of LSVEC stored at the National Institute of Standards and Technology (NIST).[17,20] The origins of these deviations are thought to be the exchange of carbon in atmospheric CO_2 with the lithium carbonate facilitated by water. Indeed, subsequent equilibration experiments have demonstrated that the carbon isotopic composition of the LSVEC material can be altered when exposed to CO_2 with a different carbon isotopic composition in a moist atmosphere.[21]

Given (i) that the original publication describing the preparation of the LSVEC material noted that it contained water[22]; (ii) that it was not packed into sealed units with an inert-gas headspace; (iii) that not all units were prepared at the same time; and (iv) that bulk containers of LSVEC material held at NIST were also been found to exhibit larger variation in carbon isotope delta than expected,[17,20] it is challenging to be certain that any particular aliquot of LSVEC reflects the exactly assigned carbon isotope-delta value and has not been the subject of isotopic exchange. It is therefore clear that the LSVEC material is unsuitable for use as a RM for carbon isotope-delta calibration. Indeed, it is no longer recommended by the IAEA or by the IUPAC CIAAW to be used as a RM for calibration of carbon isotope-delta values.[20,23,24] (The recommendation to apply two-or-more point calibration for carbon isotope delta does still remain.[23])

Instability was not the only problem uncovered with the LSVEC material. During the preparation of new carbonate RMs traceable to only NBS 19 at the IAEA,[25–27] and also at the United States Geological Survey (USGS) in collaboration with other expert laboratories,[18] the assigned carbon isotope-delta value for LSVEC was found likely to be too negative. Measurements of these new carbonate RMs traceable to NBS 19 alone against those traceable to NBS 19 and LSVEC have demonstrated a bias between the VPDB and VPDB-LSVEC scales, particularly at more negative carbon isotope-delta values.[19] These studies presented estimates of the bias between the assigned and 'true' carbon isotope-delta value for LSVEC (or between carbon isotope-delta values reported relative to NBS 19 and those relative to both NBS 19 and LSVEC) that ranged between 0.14‰[18] and approximately 0.3‰[19,20,25–27] (see Figure 3). It is difficult to determine whether the aliquots of LSVEC analysed before 2006 that led to the assignment of $\delta_{VPDB}(^{13}C/^{12}C) = -46.6‰$[7,8,13,14] had also been subject to change in carbon isotopic composition at the time of their measurement, and if so, to what extent. Naturally this might be a contributing factor to the assignment of an 'incorrect' carbon isotope-delta value for LSVEC.

With hindsight, some experts believe that the LSVEC material should never have been assigned an exact carbon isotope-delta value – but this is not a criticism of the decision taken at the time with the available information. RMs with exactly assigned isotope-delta value is a concept that should probably be avoided. Even where a material is homogeneous both between and within individual units to below the method precision, there is a component of uncertainty

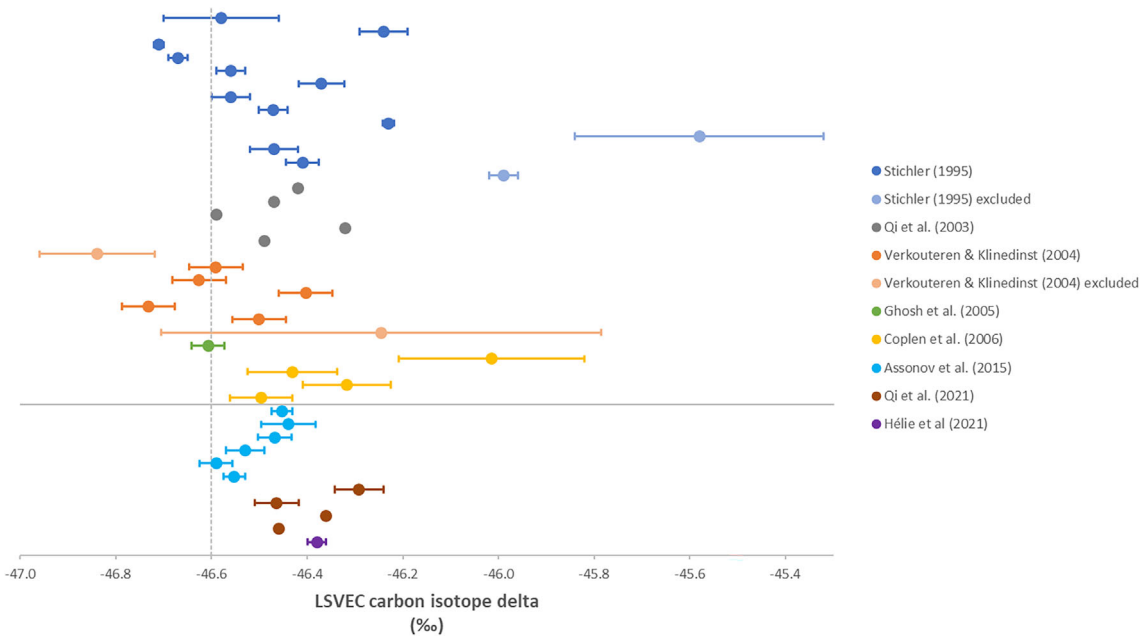

FIGURE 3 Reported measurement results for $\delta_{VPDB}(^{13}C/^{12}C)$ of the LSVEC carbonate.[8,13–18] The indirectly obtained result from Hélie et al[19] is also shown for reference. Error bars represent the standard uncertainty or standard deviations as detailed in the publications (note some values have no associated uncertainties reported). The vertical line shows the assigned value of $\delta_{VPDB}(^{13}C/^{12}C) = -46.6‰$. The horizontal line distinguishes results from before the assignment of an exact isotope-delta value from those reported since 2006 [Color figure can be viewed at wileyonlinelibrary.com]

arising from the estimation of homogeneity. While this component may be small, it is not zero and may become relevant to applications requiring uncertainties of <0.1‰. In addition, a RM with exactly assigned isotope-delta value can lead to underestimation of uncertainty when the contribution from the measurement of such a material is not included in an uncertainty budget.[28]

4 | IMPLICATIONS FOR THE VPDB-LSVEC CARBON ISOTOPE-DELTA SCALE

Generally, if a RM is found to be unsuitable to use for calibration of measurement results, for example due to previously unrecognised problems such as instability or heterogeneity, it is simply withdrawn. In those instances or should stocks of a RM begin to run low, a replacement RM may become available (for example the replacement of USGS41 by USGS41a[21]). In such cases, analysts must simply refrain from using the old material and switch to using the new one.

In this instance, however, the situation is much more complex due to the privileged position that LSVEC has held within the VPDB carbon isotope-delta scale since 2006. LSVEC is not just a RM used for calibration. Examining Figure 2 shows LSVEC in two positions: as an exactly defined point on the VPDB-LSVEC scale and as a corresponding RM that can be used for calibration of measurement results – the same is true for NBS 19 at the opposite end of the scale. Comparing LSVEC to NBS 19 and to other materials that have exactly assigned isotope-delta values may be helpful to understand some of the implications of the LSVEC problem more clearly. Such a comparison can be found in Table 1.

Carbon is not the only element with an isotope-delta scale that has more than one primary RM with exactly assigned isotope delta value; nor is it the only scale to include a virtual material. It is clear from Table 1 that LSVEC shares many characteristics with other primary RMs for other isotope-delta scales, but that none exhibit exactly the same subset. LSVEC and SLAP (for oxygen isotope delta) are the two materials with likely incorrectly assigned isotope-delta values.[30] For both LSVEC and Air-N_2 it is difficult to know whether a particular aliquot is free from inadvertent fractionation caused by isotope exchange for LSVEC, or by isolation from the atmosphere for Air-N_2.[11,31] However, it is only LSVEC that is not stable and therefore no longer sufficiently homogeneous for use as a RM, and, of the materials available for direct measurement, only LSVEC is currently prohibited from being used for calibration. It is, however, possible to obtain results traceable to any of the materials listed in Table 1 by using other RMs that have the necessary traceability to their exactly assigned isotope-delta values.

The two facets of the problem with LSVEC, namely the instability of the material itself and the likely incorrect assigned value, have various implications for the VPDB-LSVEC scale and for measurement of carbon isotope-delta values.

Firstly, the VPDB scale (as defined by Hut[6]) and the VPDB-LSVEC scale are not one and the same underlying scale with simply a different calibration requirement. They are, in fact, two separate scales and therefore carbon isotope-delta values reported on the VPDB scale will not necessarily align with those reported on the VPDB-LSVEC scale, particularly at more negative values. The magnitude of the bias is reported to be between 0.14‰[18] and approximately 0.3‰,[19,20,25–27] at carbon isotope-delta values of approximately −45‰, which may be significant depending on application. The magnitude of the bias decreases as carbon isotope-delta values tend towards zero. The bias between the two scales may be hidden where traceability chains are not reported clearly.[32] As there was no intention of creating a new scale in 2006 with the introduction of LSVEC, it is not immediately clear for some

TABLE 1 Properties of selected materials with exactly assigned isotope-delta values

	Material								
Property	**NBS 19**	**VPDB**	**LSVEC**	**VSMOW**	**SLAP**	**Air-N_2**	**USGS32**	**VCDT**	**IAEA-S-1**
Assigned $\delta = 0$		✓		✓		✓		✓	
Assigned δ is exact	✓	✓	✓	✓	✓	✓	✓[a]	✓	✓
Assigned δ is not in question	✓	✓		✓		✓	✓	✓	✓
Available as RM for direct measurement[b]	✓		✓	✓	✓		✓		✓
Currently permitted to be used for calibration	✓	n/a		✓	✓	✓	✓	n/a	✓
Sufficiently stable over time	✓	(✓)[c]		✓	✓	✓	✓	(✓)[c]	✓
Sufficiently homogeneous	✓	(✓)[c]		✓	✓	✓	✓	(✓)[c]	✓
Aliquot might not be representative of assigned value[d]			✓			✓			
RMs available that are traceable to it	✓	✓	✓	✓	✓	✓	✓	✓	✓

[a]While there is no official IUPAC recommendation that nitrogen isotope-delta values be normalised to USGS32 with $\delta_{Air\text{-}N2}(^{15}N/^{14}N) = +180‰$ exactly, it was recommended by participants in the 1993 IAEA consultants meeting,[29] and the majority of commercially available RMs are traceable to USGS32 with an exactly assigned value.[12]

[b]At some point – the material may be quarantined or exhausted at present.

[c]Virtual material and so stability and homogeneity are linked to the extant materials that define these virtual ones.

[d]Due to inadvertent fractionation during isolation/storage or from interferences during measurement.

commercial RMs to which scale their recommended values are traceable. For example, the IUPAC Technical Report on assessment of international reference materials for isotope-ratio analysis makes no distinction between values reported on the VPDB scale and those on the VPDB-LSVEC scale as it was prepared before the LSVEC problem was uncovered.[11] The updated version of this report, which is in preparation, will clearly distinguish the two carbon isotope-delta scales.

Secondly, the majority of commercially available RMs for carbon isotope delta are still traceable to the exactly assigned isotope-delta value of −46.6‰ for LSVEC. Their assigned isotope-delta values and associated uncertainties remain unchanged since the discovery of the instability of LSVEC and its withdrawl.[12] As a result, the VPDB-LSVEC scale no longer appears as depicted in Figure 2 but rather is now as shown in Figure 4. The LSVEC carbonate cannot be used directly for calibration of measurement results, so it is no longer shown, but LSVEC remains a defined point on the scale. As LSVEC cannot be used directly for calibration, it might now be considered to be virtual in the same way that VPDB cannot be used directly for calibration and is virtual. Alternatively, one might consider LSVEC in its current state to be more similar to Air-N_2 as neither is an available RM for direct use but both materials do exist.

Thirdly, future maintenance of the carbon isotope-delta scale is also affected. As described above, as LSVEC can no longer be used directly, other RMs traceable to it must be used instead. This is no different to the decades-old recommendations on use of RMs to provide traceability for measurements of isotope-delta values for virtual materials such as VPDB.[11,33] However, a problem arises when new RMs are to be characterised. Use of RMs other than LSVEC necessarily results in a longer traceability chain and consequently a larger minimum measurement uncertainty that can be achieved. For applications of carbon isotope-delta values that require the highest precision and lowest measurement uncertainty such as atmospheric greenhouse gas monitoring, this increase in uncertainty is undesirable. Calibrations using NBS 19 alone for traceability are still possible and would not be similarly affected by additional uncertainty; however, they have been shown to be biased against the VPDB-LSVEC scale. The exact magnitude of the bias is difficult to determine reliably with small uncertainty and therefore transformations from one scale to another, although possible, introduce additional uncertainty. As a result, the necessary actions for scale maintenance are not immediately clear as solutions that address the LSVEC problem while providing the ability to characterise new RMs with suitably low uncertainty are not straightforward.

That there are implications arising from the LSVEC problem can be illustrated by comparing how various publications have used LSVEC, directly or indirectly, since the instability was discovered. This is not to criticise the choices made by the authors, but simply to show that the situation has been addressed differently. Some laboratories have not analysed LSVEC directly but instead used RMs that are consistent with LSVEC having carbon isotope delta of −46.6‰ exactly (thereby consistent with Figure 3; see e.g. Schimmelmann et al[34]). Others used LSVEC itself directly but with assigned $\delta_{VPDB}(^{13}C/^{12}C) = -46.6 \pm 0.15‰$ to account for possible instability, but without this additional uncertainty being propagated into the assigned carbon isotope-delta values of the other RMs used for calibration that were themselves traceable to LSVEC (see e.g. Schimmelmann et al[35]). Finally, investigations of LSVEC by direct measurement have produced various estimates for the 'true' $\delta_{VPDB}(^{13}C/^{12}C)$ value of LSVEC of −46.46‰ and −46.36‰ (Table 1of Qi et al[18]) and of $-46.464 \pm 0.046‰$ and $-46.292 \pm 0.051‰$ (Table 9 of Qi et al[18]). Investigations that applied renormalisation of measurement data for RMs traceable to the assigned value for LSVEC but which did not involve direct analysis of LSVEC itself have also been used to provide an estimate of the 'true' $\delta_{VPDB}(^{13}C/^{12}C)$ value for LSVEC of $\delta_{VPDB}(^{13}C/^{12}C) = -46.40 \pm 0.03‰$.[19] There are clearly different approaches to continuing to use LSVEC and different estimates one could apply for the assigned value and uncertainty for LSVEC carbon isotope delta. These differences can cause bias in measurement results.

5 | POSSIBLE SOLUTIONS TO THE 'LSVEC PROBLEM'

Publications from the IAEA,[20,27] as well as from a collaboration between the USGS Reston Stable Isotope Laboratory (RSIL), the Centre for Isotope Research (CIO) at the University of Groningen, the stable isotope laboratory of the Max Planck Institute for

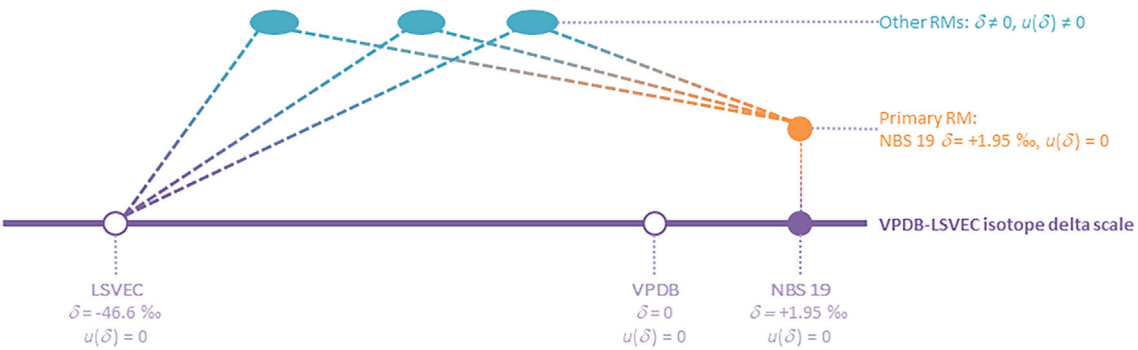

FIGURE 4 Schematic representation of the VPDB-LSVEC carbon isotope-delta scale following the withdrawal of LSVEC as a physical RM for carbon isotope delta in 2017 (not to scale) [Color figure can be viewed at wileyonlinelibrary.com]

Biogeochemistry (BGC-Isolab) and the University of Quebec at Montreal (UQAM),[18] have concurrently and independently proposed various ways to address the LSVEC problem and 'maintain' the VPDB scale for the future. Those proposals and others have been discussed by participants of the IAEA technical meetings held in 2016,[20] 2021 and 2024[36] and of the CIAAW meetings held in 2017, 2019, 2021 and 2023. Briefly, the proposals concern the VPDB and VPDB-LSVEC scales that have been confirmed to be biased against one another and whether to mandate the use of only one of them going forward or not. Each proposal is presented in more detail below.

5.1 | Proposal 1 – maintain only an unchanged VPDB-LSVEC scale

Perhaps the most straightforward option to implement is to keep LSVEC as a virtual material with an exact carbon isotope delta of $\delta_{VPDB}(^{13}C/^{12}C) = -46.6‰$. While the extant LSVEC material could not be used to realise this point, other RMs with negative carbon isotope-delta values close to the assigned value could do so – for example USGS44. Those RMs would have non-zero assigned uncertainty in their isotope-delta value. In this way, both VPDB and LSVEC would be exactly defined points on the carbon isotope-delta scale, but neither would be realised by a RM with an exactly matched carbon isotope-delta value (i.e. there would be no RM with $\delta_{VPDB}(^{13}C/^{12}C) = 0$, nor one with $\delta_{VPDB}(^{13}C/^{12}C) = -46.6‰$). Instead, the virtual LSVEC would be realised by, for example, USGS44 in the same way that the virtual VPDB is realised by NBS 19. End-users would still need to apply two-or-more point calibration. This is schematically represented in Figure 5.

This proposal is outwardly similar to the current situation for oxygen isotope-delta values traceable to VSMOW and SLAP. Several groups have reported that the exactly assigned $\delta_{VSMOW}(^{18}O/^{16}O)$ for SLAP of −55.5‰ is incorrect[14,30,37,38]; however, the conventional value is still used. As noted above, the significant difference is that SLAP does not exhibit any signs of heterogeneity or instability, unlike LSVEC, and therefore the use of SLAP as a primary RM or within a scale definition is still possible. Another similar situation exists in the field of radiocarbon dating where a conventional half-life for ^{14}C is used that is biased against the most accurately measured half-life.[39] Conventional values can afford excellent comparability between laboratories and are not necessarily things to avoid.

The two major advantages of this proposal are that the assigned/calibrated carbon isotope-delta values for existing RMs with traceability chains that end with NBS 19 and LSVEC would not require any change or reassessment; and that calibration protocols for end-users would also remain unchanged. The calibration recommendations from 2006 would still apply with the exception of not being able to use LSVEC itself directly.

This proposal would come with several significant disadvantages. Firstly, there is agreement that the assigned value of LSVEC is likely too negative by between 0.14‰[18] and approximately 0.3‰.[18–20,27] This has implications for two measurement areas. Firstly, measurements of carbon isotope delta by dual-inlet isotope ratio mass spectrometry (DI-IRMS) that rely on a single calibration point with careful consideration of cross-contamination to account for possible scale effects,[40,41] or optical spectroscopy methods that similarly use single-point calibration, will not necessarily agree with those obtained using two-point calibration, particularly at more negative carbon isotope-delta values. This will be most relevant when calibrating new RMs for carbon isotope delta. Secondly, in the rare cases when 'absolute' isotope ratios are being determined, the bias imparted by the assigned values for LSVEC being too negative will need to be considered, particularly if absolute isotope ratios are later converted to isotope-delta values.

Secondly, the RMs with carbon isotope-delta values traceable to NBS 19 alone such as the NIST CO_2 RMs (SRM 8562, 8563 and 8564), IRMM BCR-656 ethanol and BCR-657 glucose and the most recent IAEA-603, IAEA-610, IAEA-611 and IAEA-612 carbonates[26] would need re-characterisation to provide carbon isotope-delta values consistent with the VPDB-LSVEC scale. This could be achieved either by direct calibration against RMs traceable to NBS 19 and LSVEC or by correction of the apparent bias reported using a function or model such as that described by Hélie et al.[19]

Thirdly, the concept of virtual materials such as VPDB and Vienna Cañon Diablo Troilite (VCDT) can be confusing to newcomers to stable isotope analysis. That one cannot purchase VPDB in a vial for use as a calibrant is confusing enough for some. That there would be

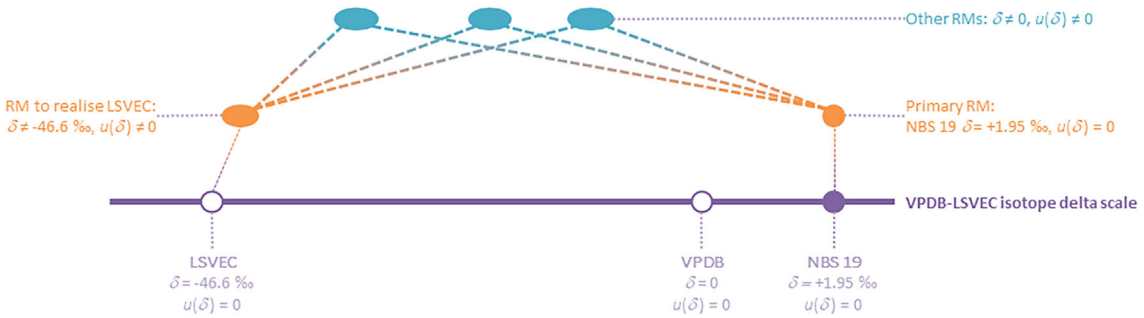

FIGURE 5 Schematic representation of proposal 1 to the 'LSVEC problem'. LSVEC is now a virtual material similar to VPDB and is realised by a RM. An example of the RM might be USGS44 or any other RM that has been calibrated to be consistent with the carbon isotope-delta value of LSVEC being −46.6‰ exactly [Color figure can be viewed at wileyonlinelibrary.com]

a second virtual RM for carbon isotope delta, called LSVEC, which also cannot be purchased for carbon isotope-delta calibration might be more confusing still; particularly when there is a RM called LSVEC that contains carbon and that can be purchased (for lithium isotopic analyses) but which should not be used for calibration of carbon isotope delta.

Fourthly, new RMs produced will no longer be able to be characterised directly against NBS 19 and LSVEC and will therefore have longer traceability chains and larger associated uncertainties. This would also occur when neither of the carbonates remained available for use.

Finally, while this is seemingly the simplest solution to the problem, it does not recognise the complexity of the situation. Nor does it highlight that assigning exact isotope-delta values to solid RMs runs the risk of potential difficulties including undiscovered heterogeneity or instability.

5.2 | Proposal 1a – maintain only the VPDB-LSVEC scale but replace LSVEC with another RM with exactly assigned carbon isotope-delta value

(This is unlikely to be implemented but is included here for completeness.)

This is very similar to Proposal 1 but selects a single RM to replace LSVEC – for example USGS44 calcium carbonate. This replacement for LSVEC would have a carbon isotope-delta value consistent with LSVEC having $\delta_{VPDB}(^{13}C/^{12}C) = -46.6‰$ and that would be exactly assigned and therefore it would become a primary RM. Both ends of the carbon isotope-delta scale would be exactly alike: PDB was replaced by the virtual VPDB which was defined by the exact carbon isotope-delta value for NBS 19; LSVEC would then be replaced by a different RM which would both define and realise exactly a point on the carbon isotope-delta scale, e.g. USGS44.

This is simple to communicate to the community and does not result in any change to calibration procedures with which analysts are familiar. However, again, it does not correct the underlying problem with the LSVEC material, nor alleviate the issue with the assigned isotope-delta value for LSVEC likely being incorrect by up to 0.3‰.

Finally, any RM with exactly assigned carbon isotope delta may be found to be unsuitable in the future despite the greatest care taken when assigning that exact value in the past or present. As this option introduces an additional RM with exactly assigned isotope-delta value, there is the risk of a similar stability problem being found with the replacement RM.

5.3 | Proposal 1b – maintain only the VPDB-LSVEC scale but alter the assigned value for LSVEC

(This is, again, unlikely to be implemented as described but is included here for completeness. Note that this proposal would provide a scale that is consistent with Proposal 2 described below.)

This is also the same as Proposal 1 with one notable change – instead of preserving the $\delta_{VPDB}(^{13}C/^{12}C) = -46.6‰$ value for LSVEC, the value assigned to LSVEC itself could be altered to reflect the bias that has since been uncovered – e.g. to something around $\delta_{VPDB}(^{13}C/^{12}C) = -46.4‰$. There would still be a replacement RM with an assigned value with associated uncertainty at the negative end of the natural abundance range (e.g. USGS44); however, the assigned value would not be consistent with the $\delta_{VPDB}(^{13}C/^{12}C) = -46.6‰$ value for LSVEC. This is shown in Figure 6.

The challenge in implementing this proposal is derivation of the 'correct' carbon isotope-delta value for LSVEC given that the material itself is unstable such that even unopened vials and bulk containers have been found to vary significantly in carbon isotope delta. Existing measurement results for LSVEC show a relatively large range of carbon isotope-delta values (Figure 3). This proposal also carries significant risk of hidden bias between isotope-delta values should carbon isotope-delta values be reported as being traceable to VPDB-LSVEC without reporting the isotope-delta value assigned to

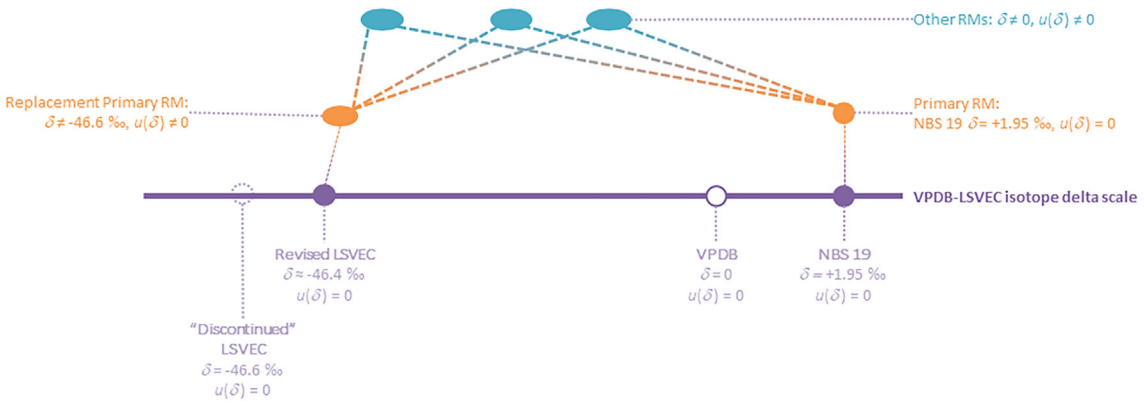

FIGURE 6 Schematic representation of Proposal 1b for the 'LSVEC problem'. The replacement primary RM would have an isotope-delta value assigned that was not consistent with LSVEC having $\delta_{VPDB}(^{13}C/^{12}C) = -46.6‰$, but rather with the best estimate of the 'correct' carbon isotope-delta value for LSVEC [Color figure can be viewed at wileyonlinelibrary.com]

LSVEC.[32] As with Proposal 1, there is still the significant potential for confusion between LSVEC as a defined point on the scale and LSVEC as a RM that cannot be used for calibration of carbon isotope delta.

This option also requires that the RMs traceable to NBS 19 and LSVEC are recalibrated to account for the change in the carbon isotope delta of LSVEC, but this could be achieved through recalculation rather than new measurements should original measurement data be available. Changing the assigned isotope-delta value of LSVEC would, however, correct the bias that the originally assigned value has introduced limiting future impacts to data comparability with approaches not based on two-point calibration and with communities using RMs with carbon isotope-delta values traceable to NBS 19 alone.

5.4 | Proposal 2 – maintain only the VPDB scale and remove LSVEC entirely

(Note that this would provide a scale that is consistent with Proposal 1b described above.)

This proposal returns to the VPDB scale as defined by Hut as the only scale for reporting carbon isotope-delta values.[6] One possible implementation of this proposal was presented by Assonov and colleagues at the IAEA[27] and involves removal of LSVEC from the scale altogether. As NBS 19 was listed as quarantined, it remains within the traceability chain as a 'historic' primary RM. The replacement for NBS 19 would be IAEA-603 (designated the 'current' primary RM). IAEA-603 is traceable directly to NBS 19 by single-point calibration using DI-IRMS with prescribed methods to correct for cross-contamination and the presence of ^{17}O. Three further carbonate RMs (IAEA-610, IAEA-611 and IAEA-612) that have been calibrated directly against IAEA-603 (again by single-point calibration using DI-IRMS) are proposed as 'scale anchor' RMs. It is envisioned that all other RMs (deemed, confusingly, 'secondary' RMs despite having more than one calibration link between them and VPDB in the traceability chain) would be traceable to VPDB through some/all of these carbonates. Secondary RMs and measurements of sample isotope-delta values still require two-or-more point calibration. This is shown in Figure 7.

This proposed scheme has a number of advantages. It affords better long-term maintenance of the VPDB scale than the 2006 version because there would be four carbonates available that could be regularly compared against each other to allow drift or instability to be detected. It also specifies the methods to be used to create further 'scale anchor' and/or 'current' primary RMs should the need arise which is a crucial aspect of scale maintenance. At least some of the pre-2006 carbon isotope-delta values, such as the assigned values for the three NIST CO_2 RMs (SRM 8562, 8563 and 8564), IRMM BCR-656 ethanol and BCR-657 glucose within the IUPAC technical report on stable isotope reference materials,[11] are consistent with this scale (i.e. the VPDB scale as defined by Hut[6] is the same scale as shown in Figure 7). For some other RMs whose carbon isotope-delta values were revised in 2006 such as NBS 22, IAEA-CH-7, IAEA-600, IAEA-601, IAEA-602, IAEA-CO-8, NBS 18, IAEA-C-3 and USGS 24, the values assigned before 2006 on the VPDB scale (as defined by Hut[6]) are available and are consistent with this new scale.[19] Moreover, there would be no arbitrary adjustments needed to future measurement data as no conventional values would be needed other than the exact carbon isotope-delta value assigned to NBS 19.

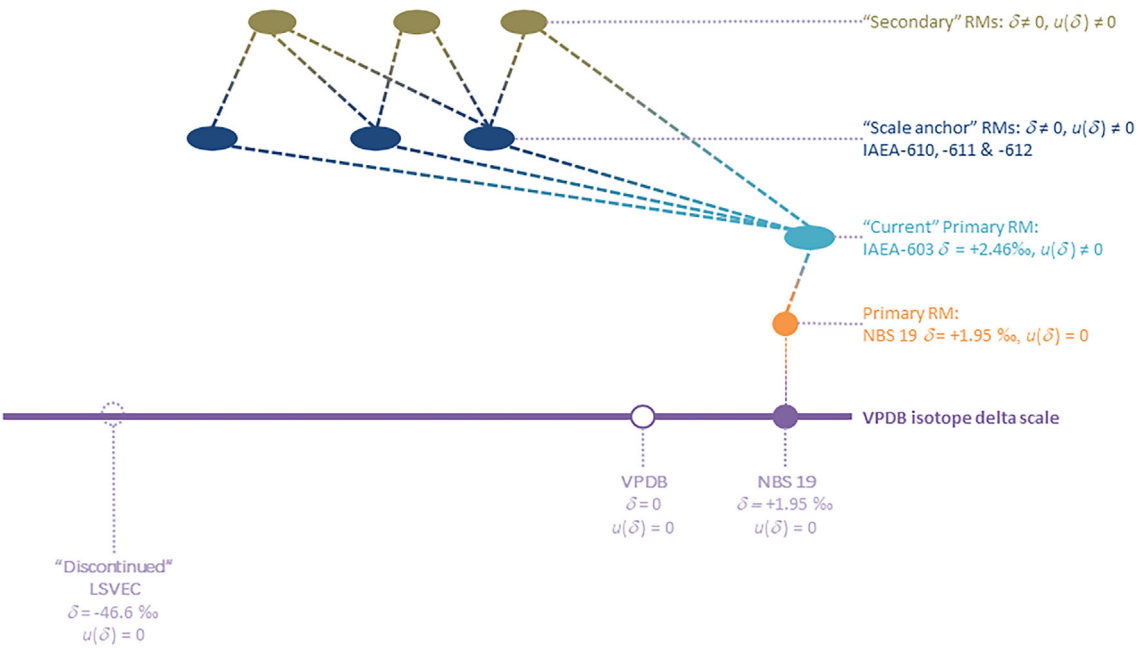

FIGURE 7 Schematic representation of Proposal 2 for the 'LSVEC problem'. RM descriptors such as 'current primary', 'scale anchor' and 'secondary' are taken from Assonov et al[27] [Color figure can be viewed at wileyonlinelibrary.com]

The major downside of this proposal concerns the bias that has become apparent between the VPDB-LSVEC scale based upon NBS 19 and LSVEC and those based upon the new suite of IAEA carbonate RMs, particularly for carbon isotope-delta values more negative than $\delta_{VPDB}(^{13}C/^{12}C) = -20‰$.[19] It is, of course, possible that measurement bias occurs for any particular set of measurements of the new suite of IAEA carbonate RMs; however, a number of different laboratories have reported broadly similar degrees of bias between carbon isotope-delta values traceable only to NBS 19 and those traceable to NBS 19 and LSVEC (see e.g. Dunn et al[12] (Table 9) and Verkouteren and Klinedinst[14]).

Adopting this new proposal therefore requires all RMs where pre-2006 data are not available to be reassessed, either through a new calibration exercise using the IAEA carbonates or, more simply, by application of a bias-correction function such as that reported by Hélie et al[19] with propagation of uncertainty. It is not immediately clear which of these approaches would result in the smallest associated measurement uncertainty. For those RMs produced following the principles of ISO 17034:2016,[42] such as NRC FRUT-1, BEET-1 and GALT-1,[43] the onus would be on the supplier to perform this reassessment. For the majority of other isotope-delta RMs, new values are sometimes proposed by third-party reassessment, re-examination of data or result from changes to reporting conventions and are then adopted more widely.[8,28,32,44,45] It is therefore not clear who would be responsible for the considerable amount of work needed to recalibrate all RMs to remove LSVEC completely from traceability chains. It is likely to involve a collaborative effort between RM suppliers and other expert laboratories.

Changing the carbon isotope-delta scale from PDB to VPDB and then the addition of LSVEC as a second calibration point both took some time for adoption among the stable isotope community. Another change to the carbon isotope-delta scale might again take many years to fully permeate the community. In the meantime, there will be significant potential for hidden bias should measurements be calibrated against RMs while assigning an older carbon isotope-delta value.[32] It is important to note that for end-users the change will simply be to the assigned value and associated uncertainty for carbon isotope-delta RMs. Such changes also occur for reasons other than a change in underlying scale, for example reassessment, and are therefore not completely unfamiliar.[32]

5.5 | Proposal 3 – do not favour one scale over the other but recognise and endorse the existence of the two different scales, VPDB and VPDB-LSVEC

This is the current situation given that most RMs have carbon isotope-delta values traceable to both NBS 19 and LSVEC while other RMs are traceable to NBS 19 alone, including the IAEA suite of carbonates, provide a subtly different scale – but one that agrees with VPDB as defined by Hut.[6] As a result, there are two scales in use concurrently that do not necessarily agree, particularly at more negative carbon isotope-delta values. Note that had LSVEC been stable, homogeneous and assigned its 'true' isotope delta value back in 2006, then there would be no difference in the VPDB scale traceable to NBS 19 alone and the VPDB-LSVEC scale traceable to NBS 19 and LSVEC and, as noted earlier, this was indeed the original intention. It is only as a result of the problems with the LSVEC material that the bias between the two scales has become apparent.

The major advantage of recognising the existence of the two scales is that there is no need for any extensive recalibration exercise, unless RM providers wish to provide carbon isotope-delta values for both scales rather than only one (very clear documentation would be required in such instances). Moreover, this proposal will guarantee consistency of the values in the communities using one or other of the scales. For example, it would allow the continuous flow IRMS community, largely using organic reference materials, to continue to use the VPDB-LSVEC scale, whereas the DI-IRMS community, often using carbonates or CO_2 reference materials, could continue to use the VPDB scale.

Carbon would not be the only element for which more than one isotope-delta scale is used. Oxygen isotope-delta values are reported on three different scales: VSMOW-SLAP, VPDB and atmospheric oxygen (Air-O_2) depending on the user community and materials being analysed. Different user communities for carbon isotope delta could similarly agree on which scale to implement. An advantage of this proposal is the opportunity to make all end-users aware that two different scales exist now – and indeed have existed since the introduction of LSVEC in 2006. That both scales share the same delta-zero point (VPDB) and a primary RM (NBS 19) might lead to somewhat more confusion than for oxygen where the zero points and primary RMs are all different between the scales. The need for careful consideration of traceability before isotope-delta values can be compared would require special emphasis.

One last advantage of this proposal is that, as it simply recognises the current situation, it does not rule out adopting one of the other proposals in the future should there be a clear need to stop using either the VPDB scale or the VPDB-LSVEC scale. The other proposals do not have this flexibility.

This proposal does come with some disadvantages, particularly in the case that two different carbon isotope-delta values are provided on RM documentation, one traceable to NBS 19 alone, the other to both NBS 19 and LSVEC (cf. the publication on USGS44 where two different carbon isotope-delta values are proposed[18]). Should this occur, there is potential for confusion amongst some users even if communicating that there are two scales makes others aware that this is the case. Some may be unsure which of the two values to use and perhaps simply pick the one with the smallest uncertainty, others may see two values and take an average – neither of which is helpful.

Moreover, should traceability for reported carbon isotope-delta values not be clear, then, as with oxygen isotope-delta values, hidden bias remains and there is potential for applying corrections when none are warranted, applying them incorrectly when they are warranted, or comparing delta values that are not comparable or compatible.[32,46] There is also a risk of users mixing RMs with assigned

values traceable to different scales within a single calibration which would lead to results that might be biased relative to both the VPDB and VPDB-LSVEC scales. Should this proposal be implemented, careful communication and provision of training will be required for users of carbon isotope-delta values.

6 | DISCUSSION

There are advantages and disadvantages to each of the proposals as described above – and we recognise that we might have missed some positive or negative implications of these proposals for particular measurement needs or application fields.

The implications of these proposals may go beyond the VPDB carbon isotope-delta scale. Addressing the bias in the assigned value of LSVEC in a particular way may pave the road for any action/revision to the VSMOW-SLAP oxygen isotope-delta scale in the light of recent measurements (even if the SLAP situation is less complex as the SLAP material is both homogeneous and stable).[30] It may impact other revisions to other isotope-delta scales in the future should issues of a similar nature arise. Any decision made cannot be taken lightly and should not be made too hastily – and indeed discussions have been taking place in the eight years since 2016. Making a similar mistake to the adoption of LSVEC now by taking a course of action to correct the LSVEC problem too quickly, which then leads to future problems should be avoided, even if it means a longer period of confusion before a solution is implemented.

It is easy with hindsight to say that adoption of LSVEC as a RM with exact carbon isotope delta was a mistake – but with the information available at the time, the LSVEC problem could not have been uncovered. Had there been an accelerated stability study of some kind for LSVEC as part of the recalibration exercise in 2006 that followed the process outlined in ISO 17034:2016[42] (and indeed has been done for IAEA-603, IAEA-610 to -612[25,26] and USGS44[18]) then perhaps the instability may have become apparent. Perhaps then LSVEC would not have been chosen to be the material with exactly assigned carbon isotope delta. As a result, we recommend that all future isotopic RMs produced commercially follow the principles of ISO 17034:2016, even though we know from experience that there are time and financial impacts from doing so.

The discussions surrounding LSVEC have also highlighted that there has been disagreement among experts regarding the differences between the definition of an isotope-delta scale and the realisation of an isotope-delta scale in practice. For example, some consider VPDB to simply be a different realisation of the PDB scale, whilst others argue that VPDB is a separate scale altogether and similarly between VPDB and VPDB-LSVEC. There has been no agreement as to whether it is NBS 19 which defines VPDB and therefore NBS 19 that is a measurement standard; or whether the measurement standard is VPDB which NBS 19 realises in practice – or, indeed, some combination of both. Similarly, there has been no agreement as to whether materials such as LSVEC, SLAP and USGS32 form part of the definition of an isotope-delta scale or are simply part of a convention for the realisation of a scale during normalisation/calibration. Even the naming conventions for the different scales have not been agreed – some prefer using VPDB and VPDB-LSVEC, while more recently, scale names such as VPDB-1987 and VPDB-2006, respectively, have been proposed.[19,27] Similarly, the nature of RMs is also in disagreement: given the complex calibration networks that exist,[12] distinction (for example 'secondary' and 'tertiary') beyond scale-defining RMs and scale-realising RMs may not be warranted. The use of 'primary' in relation to RMs is also the subject of some debate – particularly in situation where original materials have been replaced such as VSMOW and SLAP replaced by VSMOW2 and SLAP2, respectively.[47]

As noted earlier, discussions on the LSVEC problem and how to address it have been ongoing for many years within various groups. The most recent discussions occurred during the 2024 IAEA Consultancy Meetings on the Development of IAEA Stable Isotope Reference Materials and Related Products and on the Definition and Realisation of the Isotopic Delta Scales for Light Elements that took place in Vienna, Austria on 22–26 January 2024. The proposed solutions to the LSVEC problem described above were presented and once again discussed by the experts that were present who noted the various advantages and disadvantages. A detailed summary of those 2024 meetings and associated outcomes regarding the LSVEC problem can be found elsewhere.[36]

It remains essential that all method details be reported for carbon isotope-delta value determinations as described in an IUPAC Technical Report.[46] In particular the identity, assigned value and assigned uncertainty for any RMs within the traceability chain back to VPDB should be stated such that otherwise-hidden biases between carbon isotope-delta values resulting from the LSVEC problem can be detected and accounted for.[32]

AUTHOR CONTRIBUTIONS

Philip James Harris Dunn: Conceptualization; writing - original draft; investigation. **Federica Camin:** Conceptualization; writing - original draft; investigation.

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PEER REVIEW

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DATA AVAILABILITY STATEMENT

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

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