National Institute of Standards & Technology

Report of Investigation

Reference Material 8545

LSVEC

(Carbon, Oxygen, and Lithium Isotopes in Lithium Carbonate)

This Reference Material (RM) is an international measurement standard [1] that defines the isotopically light end of the Vienna PeeDee Belemnite-Li SVEC (VPDB-LSVEC) δ-scale for isotope-number ratios of carbon (C). Known isotope-number ratios for oxygen (O), lithium (Li), as well as the absolute lithium isotope-number ratio are also listed. The equivalent name for this RM, as used by the International Atomic Energy Agency (IAEA) and the U.S. Geological Survey (USGS), is LSVEC. A unit of RM 8545 consists of one bottle containing approximately 0.4 g of lithium carbonate.

Table 1. Reference Values for the Relative C, O, and Li Isotope-Number Ratios and the Absolute $^6Li/^7Li$ Isotope-Number Ratio

IAEA Name	$10^3\,\delta^{13}C_{VPDB\text{-}LSVEC}$ [(a)]	$10^3\,\delta^{18}O_{VPDB}$ [(b)]	$10^3\,\delta^{18}O_{VSMOW}$ [(b)]	$10^3\,\delta^{7}Li_{LSVEC}$ [(a)]	$^6Li/^7Li$ [(c)]
LSVEC	–46.6 exact	–26.41	+3.69	0 exact	0.08215

[(a)] The $\delta^{13}C$ and $\delta^{7}Li$ values are exact values that are used in the definitions of the VPDB and the LSVEC scales, respectively.
[(b)] This value is calculated using the relationship between VPDB and VSMOW (Vienna Standard Mean Ocean Water) on page 36 in reference 2.
[(c)] This value is an absolute isotope-number ratio [3].

Expiration of Value Assignment: RM 8545 is valid until **31 December 2020**, provided the RM is handled and stored in accordance with instructions given in this Report of Investigation (see "Instructions for Handling, Storage, and Use"). The reference values are nullified if the RM is damaged, contaminated, or otherwise modified.

Maintenance of RM: NIST will monitor this RM over the period of its validity. If substantive technical changes occur that affect the value assignment before the expiration of this report, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The technical aspects involved in the issuance of this RM were coordinated through the NIST Analytical Chemistry Division by R.D. Vocke, Jr.

Support aspects involved in the issuance of this RM were coordinated through the NIST Measurement Services Division.

Stephen A. Wise, Chief
Analytical Chemistry Division

Robert L. Watters, Jr., Chief
Measurement Services Division

Gaithersburg, MD 20899
Report Issue Date: 20 December 2011
Report Revision History on Last Page

Reference Values for the Relative Difference in Isotope-Number Ratios: The differences in measured isotope-number ratios of stable carbon isotopes [$N(^{13}C)/N(^{12}C)$], stable oxygen isotopes [$N(^{18}O)/N(^{16}O)$], and stable lithium isotopes [$N(^{7}Li)/N(^{6}Li)$] are reported as $\delta^{13}C$, $\delta^{18}O$, and $\delta^{7}Li$ values, respectively. The relative difference in isotope-number ratios for carbon, oxygen, and lithium are defined as:

$$\delta^{13}C = ([N(^{13}C)_{sample}/N(^{12}C)_{sample}] - [N(^{13}C)_{VPDB\text{-}LSVEC}/N(^{12}C)_{VPDB\text{-}LSVEC}]) / [N(^{13}C)_{VPDB\text{-}LSVEC}/N(^{12}C)_{VPDB\text{-}LSVEC}]$$

$$\delta^{18}O = ([N(^{18}O)_{sample}/N(^{16}O)_{sample}] - [N(^{18}O)_{VSMOW\text{-}SLAP}/N(^{16}O)_{VSMOW\text{-}SLAP}]) / [N(^{18}O)_{VSMOW\text{-}SLAP}/N(^{16}O)_{VSMOW\text{-}SLAP}]$$

$$\delta^{7}Li = ([N(^{7}Li)_{sample}/N(^{6}Li)_{sample}] - [N(^{7}Li)_{LSVEC}/N(^{6}Li)_{LSVEC}]) / [N(^{7}Li)_{LSVEC}/N(^{6}Li)_{LSVEC}]$$

VPDB-LSVEC refers to the Vienna PDB-LSVEC carbon δ-scale, which is defined by assigning a $\delta^{13}C$ value of + 1.95 ‰ to NBS19 Limestone (RM 8544) and a value of –46.6 ‰ to measurements of LSVEC (RM 8545) for the purpose of normalizing stable carbon isotope measurements (see "Normalization") [4–7].

VSMOW-SLAP (Standard Light Antarctic Precipitation) refers to the Vienna SMOW-SLAP δ-scale, which is defined by assigning a $\delta^{18}O$ value of 0 ‰ to VSMOW2 (RM 8535a) and a value of –55.5 ‰ to measurements of SLAP (RM 8537) for the purpose of normalizing stable oxygen isotope measurements (see "Normalization") [4–5,8].

The differences in measured isotope-number ratios of stable oxygen isotopes [$N(^{18}O)/N(^{16}O)$] in carbonates are often reported as $\delta^{18}O_{VPDB}$ values which are defined as:

$$\delta^{18}O = ([N(^{18}O)_{sample}/N(^{16}O)_{sample}] - [N(^{18}O)_{PDB}/N(^{16}O)_{PDB}])/ [N(^{18}O)_{PDB}/N(^{16}O)_{PDB}]$$

$\delta^{18}O_{VPDB}$ refers to the Vienna PDB oxygen scale, which is determined by assigning a $\delta^{18}O$ value of –2.2 ‰ to NBS19 (RM 8544) [5,8].

INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

Distribution: The distribution of RM 8545 (LSVEC) is limited to one unit per three-year period of time.

Storage and Stability: RM 8545 is stable at normal room temperatures. To minimize the potential for oxygen isotope exchange between carbonate and atmospheric water, this RM should be stored in a desiccator.

Absolute Li Isotope-Number Ratios in LSVEC: Absolute lithium isotope-number ratios have been determined for LSVEC [2] and are listed in the last column of Table 1. The measurements were made using calibrated lithium isotope mixtures and represent absolute measurements. Note that the isotopic composition of this material is statistically indistinguishable from IRMM 016, a certified lithium isotopic reference material distributed by IRMM, Belgium [2].

Sample Preparation: RM 8545 (LSVEC) was prepared by H.J. Svec, Iowa State University, Iowa, USA [9]. It was suggested as the low ^{13}C anchor for a two-point normalization of the $\delta^{13}C$ scale at an International Atomic Energy Agency (IAEA) consultants' meeting in 2004, which resulted in a subsequent recommendation by the Commission on Isotopic Abundances and Atomic Weights in August 2005 at the 43rd General Assembly of IUPAC in Beijing, PRC [6].

Normalization: The δ-values for carbon, when measured in samples, are presented as parts per thousand differences (per mill; ‰) from the VPDB δ-value normalized with the defined LSVEC δ-value. NBS19 (RM 8544) has been adopted as the anchor for the high ^{13}C end and LSVEC has been assigned a consensus value of –46.6 ‰ as the low ^{13}C end of the VPDB-LSVEC δ-scale. A general formula for normalizing carbon isotope measurement results using two laboratory standards LS1 (NBS19) and LS2 (LSVEC) can be expressed as:

$$\delta^{13}C_{sample,cal} = \delta^{13}C_{LS1,cal} + \left(\delta^{13}C_{sample,WS} - \delta^{13}C_{LS1,WS}\right) \times f \qquad (1)$$

where the normalization factor f is:

$$f = \left(\delta^{13}C_{LS2,cal} - \delta^{13}C_{LS1,cal}\right) \Big/ \left(\delta^{13}C_{LS2,WS} - \delta^{13}C_{LS1,WS}\right) \qquad (2)$$

Note: *cal* denotes calibrated measurements made versus the VPDB-LSVEC scale, and $\delta^{13}C_{LS1,cal}$ and $\delta^{13}C_{LS2,cal}$ are the conventionally fixed $\delta^{13}C$ values for NBS19 and LSVEC. *WS* denotes measurements made versus a transfer gas (working standard), $\delta^{13}C_{LS1,WS}$ and $\delta^{13}C_{LS2,WS}$ are the $\delta^{13}C$ values for calibrated laboratory working standards.

Similar formulae are used for $\delta^{18}O$. See the Report of Investigation for RMs 8535a and 8537 for further information on $\delta^{18}O$ measurements [10,11].

Reporting of Stable Isotope δ-values: The following recommendations are provided for reporting the relative difference carbon stable isotope-number ratios using the δ-notation modified from Coplen [12]; it is recommended that:

- δ^{13}C values of all carbon-bearing substances be measured and expressed relative to VPDB on a normalized scale where LSVEC has a consensus value of –46.6 ‰ and NBS19 a value of +1.95 ‰.
- Authors should clearly state that their data have been normalized.

REFERENCES

[1] JCGM 200:2008; *International Vocabulary of Metrology - Basic and General Concepts and Associated Terms (VIM)*, 3rd ed.; Joint Committee for Guides in Metrology (JCGM) (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_200_2008.pdf (accessed Dec 2011).

[2] Coplen, T.B.; Hopple, J.A.; Böhlke, J.K.; Peiser, H.S.; Rieder, S.E.; Krouse, H.R.; Rosman, K.J.R.; Ding, T.; Vocke, Jr., R.D.; Révész, K.M.; Lamberty, A.; Taylor, P.; and De Bièvre, P.; *Compilation of Minimum and Maximum Isotope Ratios of Selected Elements in Naturally Occurring Terrestrial Materials and Reagents*; U.S. Geological Survey, Water-Resources Investigations Report 01-4222, pp. 98 (2001).

[3] Qi, H.P.; Taylor, P.D.P.; De Bievre, P.; *Calibrated Measurements of the Isotopic Composition and Atomic Weight of the Natural Li Isotopic Reference Material;* IRMM-016; International Journal of Mass Spectrometry and Ion Processes, Vol. 171, pp. 263–268 (1997).

[4] Gonfiantini, R.; *Standards for Stable Isotope Measurements in Natural Compounds*; Nature, Vol. 271, pp. 534–536 (1978).

[5] Hut, G.; *Consultants' Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations*; IAEA, Vienna, Austria, 16–18 September, 1985, pp. 1–42, (1987); available at http://www-naweb.iaea.org/NAALIHL/publications3.shtml (accessed Dec 2011).

[6] Coplen, T.B.; Brand, W.A.; Gehre, M.; Groening, M.; Meijer, H.A.J.; Toman, B.; Verkouteren, R.M.; *New Guidelines for δ^{13}C Measurements*; Analytical Chemistry, Vol. 78, pp. 2439–2441 (2006).

[7] Coplen, T.B.; Brand, W.B.; Gehre, M.; Groening, M.; Meijer, H.A.J.; Toman, B.; Verkouteren, M.R.; *After Two Decades a Second Anchor for the VPDB δ^{13}C Scale;* Rapid Communications in Mass Spectrometry, Vol. 20, pp. 3165–3166 (2006).

[8] Coplen, T.B.; *Normalization of Oxygen and Hydrogen Data*; Chemical Geology, Vol. 72, pp. 293–297 (1988).

[9] Flesch, G.D.; Anderson Jr., A.R.; Svec, H.J.; *A Secondary Isotopic Standard for 6Li/7Li Determinations*; International Journal of Mass Spectrometry and Ion Physics, Vol. 12, pp. 265–272 (1973).

[10] RM 8535a; *Vienna Standard Mean Ocean Water (VSMOW2)*; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (01 October 2009); available at https://www-s.nist.gov/srmors/view_detail.cfm?srm=8535a (accessed Dec 2011).

[11] RM 8537; *SLAP—Standard Light Antarctic Precipitation (Water)*; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (03 March 2005); available at https://www-s.nist.gov/srmors/view_detail.cfm?srm=8537 (accessed Dec 2011).

[12] Coplen, T.B.; *Reporting of Stable Hydrogen, Carbon and Oxygen Isotopic Abundances*; Pure & Applied Chemistry Vol. 66, No. 2, pp. 273–276 (1994).

Report Revision History: 20 December 2011 (Updated reference values; editorial changes); 22 June 1992 (Original report date).

Users of this RM should ensure that the Report of Investigation in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.