



National Institute of Standards & Technology

Report of Investigation

Reference Materials 8562, 8563, 8564

8562: CO₂-Heavy, Paleomarine Origin (Carbon Dioxide)

8563: CO₂-Light, Petrochemical Origin (Carbon Dioxide)

8564: CO₂-Biogenic, Modern Biomass Origin (Carbon Dioxide)

These Reference Materials (RMs) are intended to provide carbon dioxide samples of known isotopic composition and uncertainty with ¹³C/¹²C and ¹⁸O/¹⁶O ratios expressed in parts per thousand relative difference (‰) from Vienna Pee Dee Belemnite (VPDB) or Vienna Standard Mean Ocean Water (VSMOW) [1]. RMs 8562, 8563, and 8564 are not certified, but their use allows comparability of stable carbon and oxygen isotope ratio data obtained by investigators in different laboratories, and provides a means to standardize laboratory gases with measurement traceability to an internationally accepted reference scale. An RM unit consists of two borosilicate glass tubes, each 9 mm in diameter and about 30 cm in length. Each tube contains approximately 400 μmol of gas and is labeled with a unique number.

Reference Values: A NIST Reference value is a non-certified value that is the best estimate of the true value; however, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may not include all sources of uncertainty. Six isotopic reference values, along with estimated expanded standard uncertainties (*U*), are provided in Table 1.

Table 1. Reference Values for $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VPDB}}$

Reference Material	$\delta^{13}\text{C}_{\text{VPDB}} \pm U^{(a)}$ (‰)	$\delta^{18}\text{O}_{\text{VPDB}} \pm U^{(a)}$ (‰)
RM 8562 (CO ₂ -Heavy)	-3.76 ± 0.07	-8.43 ± 0.44
RM 8563 (CO ₂ -Light)	-41.56 ± 0.09	-23.61 ± 0.48
RM 8564 (CO ₂ -Biogenic)	-10.45 ± 0.07	+0.06 ± 0.40

^(a) $U = ku_c$, where u_c is the combined standard uncertainty and $k = 2$ is the coverage factor [4]. Reference values are calculated on the basis of currently accepted oxygen isotope relationships, where $\lambda = 0.50$ and $K = 0.008\,332\,958\,2$ [2,3]. $\delta^{18}\text{O}_{\text{VPDB}}$ is the normalized delta value on a scale such that $\delta^{18}\text{O}_{\text{VPDB}}$ of NBS 19 $\equiv -2.2$ ‰ and $\delta^{18}\text{O}_{\text{SLAP/VSMOW}} \equiv -55.5$ ‰. [2,5].

Expiration of Reference Values: The reference values for the isotopic composition of RMs 8562, 8563, and 8564 are valid until **31 December 2017**, provided they are handled and stored in accordance with the instructions given in this report.

Maintenance of Reference Values: The isotopic compositions of these RMs are monitored on a yearly basis. If substantive changes occur to the values before expiration of this report, the National Institute of Standards and Technology (NIST) will notify the purchaser. Registration (see attached sheet) will facilitate notification.

Technical coordination for these RMs was provided by R.D. Vocke, Jr. of the NIST Analytical Chemistry Division.

Support aspects involved in the issuance of these RMs were coordinated through the NIST Measurement Services Division.

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INSTRUCTIONS FOR USE

Storage and Use: Until use, it is recommended that these RMs be stored in their original container at ambient temperature (20 °C to 30 °C). Before use, the user's inlet system should be conditioned with carbon dioxide of isotopic composition similar to the RM. To open, the RM requires the proper use of a suitable tube cracker [e.g., 6-9], and after opening should be used immediately for calibration or standardization. If desired, a sample can be stored in a clean glass breakseal or container fabricated with an all-glass stopcock coated with a hydrocarbon-based grease, or other vessel known to preserve the isotopic integrity of carbon dioxide [10].

NOTE: Because very limited quantities of these materials exist, distribution is limited to one unit (two tubes) of each RM per three-year period. Users are strongly advised to prepare their own internal standards for routine quality control and to normalize or compare those standards with these RMs.

PREPARATION AND ANALYSIS

Preparation: RMs 8562, 8563, and 8564 were prepared by R.M. Verkouteren of the Surface and Microanalysis Science Division. Details of the preparation method are published in reference 11. RM 8562 was prepared in 1995 from carbon dioxide provided by T. B. Coplen, U.S. Geological Survey (USGS) (Reston, VA, USA). This gas originated from natural thermal decomposition of a Jurassic limestone deposit in the Southeastern United States [12], and was sampled through a well in 1982. RM 8563 was prepared in 1996 from SFE-grade carbon dioxide (99.999 % molar purity) obtained through Scott Specialty Gase (Plumsteadville, PA). This gas originated from combustion of byproducts from a petrochemical refinery in the Eastern United States. Lastly, RM 8564 was prepared in 1996 from research grade carbon dioxide (99.995 % molar purity) obtained through Scott Specialty Gases (Plumsteadville, PA). This gas originated from the fermentation of C4 biomass (corn) in a grain distillery in the Central United States.

Isotopic Uniformity: After production, the RM tubes were heated to 70 °C for 24 hours to accelerate potential isotopic exchange of carbon dioxide with trace water vapor or the silicate interior of the tubes, then were allowed to incubate for at least one month before the batch was characterized. Determination of the isotopic heterogeneity of each RM batch was facilitated through a uniform sampling design, where samples were selected for measurement (through their unique identifier) to explore the effects of inherent nuisance factors documented during RM production; fortunately, no factors were significant. Measurements on RM 8562 and RM 8563 were performed at NIST, while measurements on RM 8564 were performed at USGS. No datum was excluded as a statistical outlier. Observed isotopic variability was apportioned between instrumental effects and true sample-to-sample heterogeneity.

Table 2. Isotopic Variations in CO₂ Reference Materials

Reference Material	Estimated RM Variation in $\delta^{13}\text{C}$ (sample-to-sample heterogeneity, $\pm U^{(a)}$) (‰)	Estimated RM Variation in $\delta^{18}\text{O}$ (sample-to-sample heterogeneity, $\pm U^{(a)}$) (‰)
RM 8562 (n=44)	0.0073 \pm 0.0029	0.0253 \pm 0.0070
RM 8563 (n=50)	0.0039 \pm 0.0039	0.0134 \pm 0.0037
RM 8564 (n=43)	0.0044 \pm 0.0085	0.0183 \pm 0.0116

^(a) Expanded uncertainties, U , of the variation estimates are symmetric 95 % confidence levels.

Analytical Methods: Reference values for the RMs were determined using one method by outside collaborating laboratories and a different method at NIST [2,13]. The Light Stable Isotope Working Group (convened by the International Atomic Energy Agency) designed a comparison exercise, where each participating laboratory was selected by virtue of proven expertise on isotope ratio mass spectrometers of different manufacturers and models. This allowed representative and equal coverage of uncertainty from different instruments. Each laboratory was requested to measure a specific sequence of samples, which in addition to the subject materials included CO₂ generated from carbonate and water RMs using specified procedures. Each laboratory then reported background corrected $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ measurements against their machine working gas. At NIST, the measurements were validated, corrected for cross contamination, and converted to standardized $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values using international conventions. With respect to the prior assignment of RMs 8562-8564, delta assignments were essentially unchanged for $\delta^{13}\text{C}$ but shifted to more negative values for $\delta^{18}\text{O}$, reflecting the correction for cross contamination and the use of standard chemical and data handling procedures.

To independently assign values and uncertainties, NIST measured the differences in delta values ($\Delta\delta^{45}\text{CO}_2$ and $\Delta\delta^{46}\text{CO}_2$) between the RMs, where a high-accuracy method was employed [11]. This method utilized the measurement of $\delta^{47}\text{CO}_2$ along with $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$. The $\delta^{47}\text{CO}_2$ value *measured* was similar to the $\delta^{47}\text{CO}_2$ value *expected* (as calculated from $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$) only when all three measurements were accurate, a condition satisfied by atypical measurement procedures involving long inlet equilibration times, minimal accelerating voltage, and maximized ion source conductance. Because $\delta^{13}\text{C}_{\text{VPDB}}$ intercomparison results for RM 8562 were the most precise, this material was used as the basis in calculating the assigned $\delta^{13}\text{C}_{\text{VPDB}}$ values for the other two RMs using the $\Delta\delta^{45}\text{CO}_2$ and $\Delta\delta^{46}\text{CO}_2$ measurements. For $\delta^{18}\text{O}_{\text{VPDB}}$, RM 8564 intercomparison results were most precise, so this RM provided the basis for $\delta^{18}\text{O}_{\text{VPDB}}$ values of the other RMs. In all cases, the value assignments were within the uncertainties of the mean values observed in the intercomparison.

Data Handling Procedures: A website is available at <http://www.nist.gov/widps-co2> to aid in data standardization, reduction, and normalization [14]. These RMs may be used to determine normalized $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of a laboratory reference gas (LRG) through interpolation using the equation below [1], where δ^m values are measured or assigned $\delta^{13}\text{C}$ ($m=13$) or $\delta^{18}\text{O}$ ($m=18$) values for two RMs (RM1 and RM2) that bracket the composition of the LRG. Upon establishing the normalized composition of at least two LRGs, these in turn may be used routinely to determine the normalized compositions of samples. When reporting normalized delta values of samples, the assigned values of the RMs should also be reported.

$$\delta_{\text{LRG.normalized}}^m = \delta_{\text{RM1.assigned}}^m + \left[\frac{\delta_{\text{LRG.measured}}^m - \delta_{\text{RM1.measured}}^m}{\delta_{\text{RM2.measured}}^m - \delta_{\text{RM1.measured}}^m} \right] \times \left[\delta_{\text{RM2.assigned}}^m - \delta_{\text{RM1.assigned}}^m \right]$$

$\delta^{18}\text{O}_{\text{VPDB}}$ values may be expressed versus VSMOW or VPDB- CO_2 through the following conversion formulae:

$$\delta^{18}\text{O}_{\text{VSMOW}} = 1.03092 \times \delta^{18}\text{O}_{\text{VPDB}} + 30.92$$

$$\delta^{18}\text{O}_{\text{VPDB-CO}_2} = (\delta^{18}\text{O}_{\text{VPDB}} - 10.25) / 1.01025$$

SUPPLEMENTAL INFORMATION

Absolute Ratios: The absolute isotope ratios of $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$, reported in standard reference artifacts, are summarized in Table 3. The precisions of the values reported are not justified by their uncertainties, but rather by the requirement of consistency of their “accepted values” used in data reduction algorithms for high-precision intercomparability of standardized $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values.

Table 3. Absolute ^{13}C and ^{18}O Abundances in Standard Reference Artifacts

Standard Reference Artifact	$^{13}\text{C}/^{12}\text{C} \pm U^{(a)}$	$^{18}\text{O}/^{16}\text{O} \pm U^{(a)}$	Reference
PDB-Chicago	$(11\,237.2 \pm 60) \times 10^{-6}$	N/A	[15]
RM 8544 (NBS19)	$(11\,201.5 \pm 28) \times 10^{-6}$	N/A	[16]
RM 8535 (VSMOW)	N/A	$(2005.20 \pm 0.45) \times 10^{-6}$	[17]

^(a) $U = ku_c$, where u_c is the reported combined standard uncertainty and $k = 2$ is the coverage factor [4].

Traceability: VPDB is the accepted “stated reference” [18] of the $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ isotope ratio measurement traceability chains, and VPDB is realized primarily and explicitly through the limestone RM 8544 (NBS19), where:

$$\text{NBS19-limestone: } \delta^{13}\text{C}_{\text{VPDB}} \equiv +1.95 \text{ ‰}, \delta^{18}\text{O}_{\text{VPDB}} \equiv -2.20 \text{ ‰} \quad [1]$$

For carbon dioxide generated from NBS19-limestone, using 100 % phosphoric acid and assuming an oxygen isotope fractionation factor of 1.01025 (at 25.0 °C):

$$\text{NBS19-CO}_2: \delta^{13}\text{C}_{\text{VPDB}} = +1.95 \text{ ‰}, \delta^{18}\text{O}_{\text{VPDB}} = +8.03 \text{ ‰} \quad [1]$$

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Users of these RMs should ensure that the Report of Investigation in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at <http://www.nist.gov/srm>.