



National Institute of Standards & Technology

Report of Investigation

Reference Material 8562

CO₂-¹³C-enriched, Paleomarine Origin (Carbon Dioxide)

This Reference Material (RM) provides carbon dioxide samples of known isotopic composition and uncertainty for measuring relative differences in stable carbon (C) isotope ratios, $R(^{13}\text{C}/^{12}\text{C})$, and stable oxygen (O) isotope ratios, $R(^{18}\text{O}/^{16}\text{O})$. While the values reported for this RM are not certified, their use will improve the comparability of stable carbon and oxygen isotope ratio data measured in different laboratories, as well as a means to standardize laboratory gases with measurement traceability to the internationally accepted isotopic reference scales, Vienna Pee Dee Belemnite (VPDB) and Vienna Standard Mean Ocean Water (VSMOW) [1]. Values given in this report are expressed relative to VPDB. A RM unit consists of two borosilicate glass tubes, each 9 mm in diameter and approximately 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 a best estimate of the true value; however, the value does not meet NIST criteria for certification and is provided with an associated uncertainty that may not include all sources of uncertainty [2].

Table 1. Reference Values for Carbon and Oxygen Isotopes in RM 8562, CO₂-¹³C-enriched, Paleomarine Origin

Analyte	Reference Value (‰)
$\delta^{13}\text{C}_{\text{VPDB}}^{(a)}$	-3.72 ± 0.07
$\delta^{18}\text{O}_{\text{VPDB}}^{(a)}$	-8.43 ± 0.44

^(a) The $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VPDB}}$ values are expressed as means with associated expanded uncertainties. Each expanded uncertainty is equal to $U = k u_c$, where u_c is the combined standard uncertainty and k is the coverage factor, as defined in the ISO/JCGM Guide [3]. For these values, the coverage factor, $k = 2$, provides an expanded uncertainty interval that has about a 95 % probability of encompassing the true value.

Expiration of Reference Values: RM 8562 is valid, within the measurement uncertainty specified, until **31 December 2027**, provided the RM is handled and stored in accordance with the instructions given in this Report of Investigation (see “Instructions for Storage and Use”). The report is 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 expiration of this report, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Technical coordination for this RM is provided by R.A. Kraft of the NIST Chemical Sciences Division.

This material was prepared by T.B. Coplen, U.S. Geological Survey (USGS, Reston, VA).

Coordination of the technical measurements leading to the certification of this material was performed by R.M. Verkouteren of the NIST Materials Measurement Science Division.

Support aspects involved in the issuance of this RM was coordinated through the NIST Office of Reference Materials.

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Relative Difference in Isotope Ratio Values: The differences in measured isotope ratios of stable carbon isotopes [$N(^{13}\text{C})/N(^{12}\text{C})$] are reported as $\delta^{13}\text{C}_{\text{VPDB}}$ values, where:

$$\delta^{13}\text{C}_{\text{VPDB}} = \frac{\left[\frac{N_{\text{sample}}(^{13}\text{C})}{N_{\text{sample}}(^{12}\text{C})} \right] - \left[\frac{N_{\text{VPDB}}(^{13}\text{C})}{N_{\text{VPDB}}(^{12}\text{C})} \right]}{\left[\frac{N_{\text{VPDB}}(^{13}\text{C})}{N_{\text{VPDB}}(^{12}\text{C})} \right]}$$

The VPDB scale is determined by assigning a $\delta^{13}\text{C}$ value of +1.95 ‰ to RM 8544 *NBS 19 Limestone* [1,4]. The differences in measured isotope-number ratios of stable oxygen isotopes [$N(^{18}\text{O})/N(^{16}\text{O})$] in carbonates and this RM are reported relative to VPDB, where:

$$\delta^{18}\text{O}_{\text{VPDB}} = \frac{\left[\frac{N_{\text{sample}}(^{18}\text{O})}{N_{\text{sample}}(^{16}\text{O})} \right] - \left[\frac{N_{\text{VPDB}}(^{18}\text{O})}{N_{\text{VPDB}}(^{16}\text{O})} \right]}{\left[\frac{N_{\text{VPDB}}(^{18}\text{O})}{N_{\text{VPDB}}(^{16}\text{O})} \right]}$$

The $\delta^{18}\text{O}_{\text{VPDB}}$ values are calculated using currently accepted oxygen isotope relationships, where $\lambda = 0.50$ and $K = 0.008\ 332\ 958\ 2$ [3]. $\delta^{18}\text{O}_{\text{VPDB}}$ is the normalized delta value on a scale such that $\delta^{18}\text{O}_{\text{VPDB}}$ of RM 8544 $\equiv -2.2$ ‰ when $\delta^{18}\text{O}_{\text{SLAP/VSMOW}} \equiv -55.5$ ‰.

INSTRUCTIONS FOR STORAGE AND USE

Storage and Use: Until use, it is recommended that this RM be stored in its original container at ambient temperature (20 °C to 30 °C). Before use, the user's inlet system should be conditioned with carbon dioxide of an isotopic composition similar to this RM. To open this RM requires the proper use of a suitable tube cracker [5-8], and once opened should be used immediately for calibration or standardization. If desired, a sample of the gas 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 [9].

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

PREPARATION AND ANALYSIS⁽¹⁾

Preparation: RM 8562 was prepared and provided by USGS in 1995. This gas originated from thermal decomposition of a Jurassic limestone deposit in the southeastern United States [10-11].

Analytical Methods: The reference values for RM 8562 (as well as for RMs 8563 and 8564) were determined in an interlaboratory comparison exercise using one method by the external collaborating laboratories and a different method at NIST [2]. The Light Stable Isotope Working Group (convened by the International Atomic Energy Agency) designed this comparison exercise, where each participating laboratory was selected based on proven expertise on isotope ratio mass spectrometers from different manufacturers. This design allowed representative and equal coverage of potential biases arising from different instruments. Each laboratory was requested to measure a specific sequence of samples, which in addition to the subject materials included CO_2 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 working gases. The measurements were subsequently validated, corrected for cross contamination, and converted to standardized $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VPDB}}$ values using international conventions.

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 RMs 8562, 8563 and 8564, where a high-accuracy method was employed [10]. 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 $\delta^{47}\text{CO}_2$ values *measured* were similar to the $\delta^{47}\text{CO}_2$ values *expected* (as calculated from $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$) only when all three measurements were accurate and consistent, a condition satisfied by atypical measurement procedures involving long inlet equilibration times, minimal accelerating voltage, and maximized ion source conductance. The $\delta^{13}\text{C}_{\text{VPDB}}$ intercomparison results for

⁽¹⁾ Certain commercial equipment, instruments, or materials are identified in this report to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

RM 8562 were the most precise; therefore, this material was used as the basis for 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 the most precise, so this RM provided the basis for the $\delta^{18}\text{O}_{\text{VPDB}}$ values for the other RMs. In all cases, the value assignments were within the uncertainties of the mean values observed from the intercomparison.

Data Handling Procedures: This RM, in conjunction with the other RMs in this series (8563 and 8564), 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 values ($\delta^{13}\text{C}$ (m=13) or $\delta^{18}\text{O}$ (m=18)) for two different RMs (RM1 and RM2) that bracket the composition of the LRG.

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

Upon establishing the normalized compositions of at least two LRGs, these gases may in turn be used to routinely determine the normalized compositions of samples. When reporting normalized delta values of samples, the assigned values of the RMs should also be reported.

$\delta^{18}\text{O}_{\text{VPDB}}$ values may be expressed versus VSMOW through the following conversion formulae [12-14]:

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

Metrological Traceability: VPDB is the accepted “stated reference” [15] 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, where:

$$\text{RM 8544 NBS19 Limestone: } \delta^{13}\text{C}_{\text{VPDB}} \equiv +1.95 \text{ ‰; } \delta^{18}\text{O}_{\text{VPDB}} \equiv -2.20 \text{ ‰}$$

For carbon dioxide generated from RM 8544, using 100 % phosphoric acid and assuming an oxygen isotope fractionation factor of 1.01025 (at 25.0 °C):

$$\text{RM 8544-CO}_2: \delta^{13}\text{C}_{\text{VPDB}} = +1.95 \text{ ‰; } \delta^{18}\text{O}_{\text{VPDB}} = +8.03 \text{ ‰}$$

Participants in RMs 8562-8564 Interlaboratory Comparison Exercise:

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REFERENCES

- [1] Coplen, T.B.; *Guidelines and Recommended Terms for Expression of Stable-Isotope-Ratio and Gas-Ratio Measurement Results*; Rapid Communications in Mass Spectrometry, Vol. 25, pp. 2538–2560 (2011).
- [2] May, W.; Parris, R.; Beck II, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260-136; U.S. Government Printing Office: Washington, DC (2000); available at: <https://www.nist.gov/srm/publications.cfm> (accessed July 2018).
- [3] JCGM 100:2008; *Guide to the Expression of Uncertainty in Measurement*; (GUM 1995 with Minor Corrections), Joint Committee for Guides in Metrology (JCGM) (2008); available at http://www.bipm.org/utis/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed July 2018); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at <https://www.nist.gov/pml/nist-technical-note-1297> (accessed July 2018).
- [4] Allison, C.E.; Francey, R.J.; Meijer, H.A.J.; *Recommendations for the Reporting of Stable Isotope Measurements of Carbon and Oxygen in CO₂ Gas: Reference and Intercomparison Materials for Stable Isotopes of Light Elements*, International Atomic Energy Agency-Technical Documents, IAEA TECDOC-825, pp. 155–162 (1995).
- [5] DesMarais, D.J.; Hayes, J.M.; *Tube Cracker for Opening Glass-Sealed Ampoules under Vacuum*; Analytical Chemistry, Vol. 48, pp. 1651–1652 (1976).
- [6] Coleman, D.D.; *Tube Cracker for Opening Samples Sealed in Glass Tubing*; Analytical Chemistry, Vol. 53, pp. 1962–1963 (1981).
- [7] Caldwell, W.E.; Odom, J.D.; Williams, D.F.; *Glass-Sample Tube Breaker*; Analytical Chemistry, Vol. 55, pp. 1175–1176 (1983).
- [8] Kennedy, H.; Kennedy, D.P.; *Simplified Tube Cracker for Opening Samples Sealed in Glass Tubes While Under Vacuum*; Analytical Proceedings including Analytical Communications, Vol. 31, pp. 299–300 (1994).
- [9] Revesz, K.; Coplen, T.B.; *Caution on the Use of Viton or FETFE O-Rings in Carbon Dioxide Sample Containers for $\delta^{18}\text{O}$ Analysis*; Chemical Geology (Isotope Geoscience Section), Vol. 86, pp. 259–261 (1991).
- [10] Verkouteren, R.M.; *Preparation and Characterization of Carbon Dioxide Isotopic Reference Materials: RMs 8562–8564*; Analytical Chemistry, Vol. 71, pp. 4740–4746 (1999).
- [11] Studlick, J.R.J.; Shew, R.D.; Basye, G.L.; Ray, J.R.; *A Giant Carbon Dioxide Accumulation in the Norphlet Formation, Pisgah Anticline, Mississippi*; Sandstone Petroleum Reservoirs, Ed.: Barwis, J.H.; McPherson, J.G.; Studlick JR, Springer-Verlag; NY, 1990, pp.181–203.
- [12] Coplen, T.B.; *Normalization of Oxygen and Hydrogen Isotope Data*; Chemical Geology (Isotope Geoscience Section), Vol. 72, pp. 293–297 (1988).
- [13] Gonfiantini, R.; *Advisory Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations*, Vienna, 19–21 September 1983, Report to Director General, International Atomic Energy Agency, Vienna.
- [14] Hut, G.; *Consultants' Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations*, Vienna, 16–18 September 1985, Report to Director General, International Atomic Energy Agency, Vienna.
- [15] JCGM 200:2012; *International Vocabulary of Basic and General Terms in Metrology*, International Organization for Standardization, VIM, 3rd edition, (2008 version with minor corrections) Geneva, Switzerland, available at https://www.bipm.org/utis/common/documents/jcgm/JCGM_200_2012.pdf (accessed July 2018).

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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 at: telephone (301) 975-2200, fax (301) 948-3730, e-mail srminfo@nist.gov, or via the Internet <https://www.nist.gov/srm>.