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2004 Edition

Standard Reference Materials[®]

**Value Assignment and Uncertainty Estimation of
Selected Light Stable Isotope Reference Materials:
RMs 8543-8545, RMs 8562-8564, and RM 8566**

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Value Assignment and Uncertainty Estimation of Selected Light Stable Isotope Reference Materials: RMs 8543-8545, RMs 8562-8564, and RM 8566

Abstract. We report the technical basis for value assignments of several carbon and oxygen stable isotope reference materials distributed by NIST and the International Atomic Energy Agency (IAEA), and make recommendations regarding laboratory practices and future intercomparison exercises. Assignments and estimates of uncertainty are based on measurement data using one method at NIST and another method at outside collaborating laboratories. All methods are based on isotope ratio mass spectrometry (IRMS) of carbon dioxide: outside collaborators measured three isobaric forms of CO₂, whereas NIST measured four forms. This additional capability allowed NIST to assess measurement accuracy, and design an IRMS method that minimized bias from cross-contamination.

The international comparison exercise was designed, involving standard chemical preparation and isotopic measurement — under strict requirements designed by the IAEA-Working Group for Reference Materials — of CO₂ derived from carbonates, waters, and pure CO₂ reference materials. Our goal was to determine precise $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ value assignments that were consistent across the materials and corrected for cross-contamination, and to relate variations in results with specific laboratory practices to guide future intercomparisons. Measurement data from all participants were compiled in a spreadsheet and inspected for consistency. Those data meeting the performance requirements were corrected for cross-contamination through direct measurement of this effect, then processed using internationally accepted procedures to determine standardized $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. For the carbonate and CO₂ materials, the results of this intercomparison provide value assignments shifted slightly towards more depleted compositions with uncertainties improved by factors up to two over the previous assignments. For the water materials, results were more variable yet suggested that the $\delta^{18}\text{O}$ value of SLAP on the VSMOW isotope ratio scale is between -55.7‰ and -56.2‰ . When normalized, $\delta^{18}\text{O}$ values were consistent with prior determinations. Statistical approaches were used to discern relationships between results and discretionary factors; these relationships are described.

To investigate the effects of oxygen isotope compositional assumptions used in data processing, several sets of assumptions were applied. Results are compared and recommendations made regarding the use of these assumptions and the effect on intercomparability of data.

Keywords: carbon dioxide; carbon isotopes; carbonates; cross contamination; intercomparison; IRMS; multivariate analysis; normalization; oxygen isotopes; performance metrics; standardization; traceability

¹ This revision reflects changes to the assigned oxygen isotope values and uncertainties on Table 8, modifies the last two footnotes of Table 8, and adds references to normalization procedures on page 11.

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The NIST-IAEA Measurement Intercomparison of Carbon and Oxygen Stable Isotope Reference Materials was made possible by the support and exceptional work of many people. We acknowledge especially the Hydrology Section of the IAEA and the Standard Reference Materials Program at NIST for their active interest and support for the project. We especially wish to thank Manfred Groening (IAEA), Nancy Trahey (formerly at SRMP-NIST), and Harro A.J. Meijer (CIO) for their leadership in enabling this exercise.

The participants of this intercomparison exercise (Table 1) are most gratefully recognized for their substantial and *pro bono* efforts, as well as discussions, comments, and post-exercise feedback that have led to this report. Their involvement has been crucial to the advancement of the stable isotope metrology activities of the IAEA and NIST, which in turn support and benefit isotope measurement communities worldwide.

The IAEA Working Group at the 1998 and 2000 meetings did a commendable job in conceiving and designing this exercise, which included identifying and balancing the control of important variables against the technical practicalities of the measurements. This group included Colin Allison, S. K. Bhattacharya, Tyler Coplen, Paul DeBièvre, Tiping Ding, Matthias Gehre, Roberto Gonfiantini, Manfred Groening, Stanislaw Halas, Donna Klinedinst, Harro Meijer, Willem Mook, Rolf Neubert, Gerhard Strauch, Philip Taylor, and Mike Verkouteren.

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Acronyms, Terms, and Symbols

CCM. Cross-contamination Model. See explanation under the symbol η .

CIO. The Center for Isotope Research (Centrum voor IsotopenOnderzoek) is an interdisciplinary research institute within the University of Groningen. The center has a long and distinguished history in measurements and standards activities regarding the natural abundances and variations in rare isotopes.

GS-40. Groningen Standard 40, an isotopically-enhanced pure CO₂ with nominal composition of $\delta^{13}\text{C}_{\text{VPDB}} \approx +1000 \text{‰}$ (2 ‰ ¹³C) and $\delta^{18}\text{O}_{\text{VPDB.CO2}} \approx +2000 \text{‰}$ (0.8 ‰ ¹⁸O). Prepared by H.A.J. Meijer and R. Neubert of CIO, Groningen. GS-40 was used to determine the level of cross-contamination in each participating instrument through Eq. 5 (see text).

IAEA. International Atomic Energy Agency. The IAEA serves as the world's foremost intergovernmental forum for scientific and technical co-operation in the peaceful use of nuclear technology. The IAEA Hydrology Section serves the needs of 130 Member States through the Light Stable Isotope Programme, which includes standards activities as well as measurement and training services.

IRMS. Isotope Ratio Mass Spectrometry, which for gases may be differentiated into three modes: absolute IRMS, dual-inlet IRMS, and continuous-flow IRMS (or isotope ratio monitoring IRMS). Absolute IRMS, with the aid of small correction factors, measures absolute abundance ratios, albeit with limited precision. Dual-inlet IRMS measures the isotopic difference between two gases with high precision. In this work, we used this mode exclusively, where all isotopic compositions were effectively referenced against the gas NBS19-CO₂. The third mode, continuous-flow IRMS, requires much less sample (and time) than dual-inlet IRMS, but is less precise. Continuous-flow IRMS involves on-line chemical separation techniques, such as Gas Chromatography-Combustion (GCC-IRMS) or Elemental Analysis (EA-IRMS).

Isotopomers. Molecules distinguished by having a particular isotopic mass. ¹⁶O¹²C¹⁷O and ¹⁶O¹³C¹⁶O are both mass 45 isotopomers of CO₂.

LSVEC. Li₂CO₃ isotope reference material (NIST RM 8545) originally prepared by H. Svec, Iowa State University.

LSG. Laboratory Standard Gas. Each laboratory had discretion to use a LSG of any composition, although we suggested a pure CO₂ similar to their working reference gas (WRG). Samples of LSG were part of the sample analysis sequence.

m/z. Mass-to-Charge ratio.

NBS19. RM 8544 limestone. This primary reference material is used to realize the VPDB isotope ratio scale, where $\delta^{13}\text{C}_{\text{NBS19/VPDB}} \equiv +1.95 \text{‰}$ and $\delta^{18}\text{O}_{\text{NBS19/VPDB}} \equiv -2.20 \text{‰}$

NBS19-CO₂ or NBS19.CO2. The CO₂ derived from NBS19 through digestion in 100% H₃PO₄ at 25 °C, where the isotopic fractionation factor $\alpha_{\text{CO}_2\text{-limestone}} = 1.01025$ for ¹⁸O/¹⁶O, and unity for ¹³C/¹²C.

NIST. National Institute of Standards and Technology, formerly known as the National Bureau of Standards (NBS). NIST is a non-regulatory federal agency in the U.S. Department of

Commerce, with responsibility for developing, maintaining and disseminating fundamental metrology to benefit industry and improve the quality of life. NIST programs include international standards activities that impact this mission.

PCA. Principal Components Analysis, which is a technique for reducing complex multivariate data to fewer, more easily interpretable dimensions. In this work, we used PCA to determine the significance of unrestricted variables on the results of the intercomparison exercise.

RM. Reference Material, often numbered to identify a particular material. Value assignments (and associated uncertainties) of RMs are not certified, but are the best values based on current knowledge.

SLAP. Standard Light Antarctic Precipitation (NIST RM 8537 water) obtained from a South Pole firm sample collected by E. Picciotto, Université Libre de Bruxelles, at Plateau Station, Antarctica in 1967.

SRM.[®] Standard Reference Material, designating a material having stated properties as certified by NIST. Presently, SRM-status is pending on several of the materials investigated through this exercise.

VPDB. Vienna-PeeDee Belemnite. The internationally-accepted isotope ratio scale, primarily realized through RM 8544 (NBS 19), for reporting relative ¹³C and ¹⁸O measurements through the *delta* (δ) notation. Also, the name given to the conceptual (but non-existent) reference artefact that defines the VPDB carbon and oxygen isotope ratio scales.

VPDB-CO₂ or VPDB.CO2. The isotope ratio scale based on CO₂ derived from the conceptual artefact VPDB, where the internationally-accepted isotopic fractionation factor $\alpha_{\text{CO}_2\text{-calcite}} = 1.01025$ for equilibration of ¹⁸O abundance at 25 °C, and unity for ¹³C abundance.

VSMOW. Vienna Standard Mean Ocean Water. The internationally-accepted isotope ratio scale for reporting relative ¹⁸O and deuterium measurements through the *delta* (δ) notation. Also, the name given to the reference water (NIST RM 8535) that defines the VSMOW hydrogen and oxygen isotope ratio scales.

VSMOW-CO₂ or VSMOW.CO2. The isotope ratio scale based on CO₂ derived from VSMOW, where the internationally-accepted isotopic fractionation factor $\alpha_{\text{CO}_2\text{-H}_2\text{O}} = 1.0412$ for equilibration of ¹⁸O abundance at 25 °C.

WRG. Working Reference Gas, also known as the Working Machine Gas (WMG), which is used on the “Standard” or Reference side (and introduced via Inlet 2) of a dual inlet IRMS system to provide a common measurement reference for samples (introduced via Inlet 1) in the sequence of analyses. The composition of the WRG was an unrestricted variable in each laboratory.

WMG. See WRG

Z and ΔZ . Voltage ratio, and difference between two voltage ratios. Here, used to measure the degree of stability of ion source conditions (Eq. 4), and to determine the cross-contamination effect through Eq. 5 (see text).

- δ . The symbol *delta*. A dimensionless quantity used to express the value of an isotope ratio (R) in a sample relative to a stated reference (Equation 1), where the m term designates the minor isotope or isotopomers in the ratio considered (e.g., $m = 13$ for $^{13}\text{C}/^{12}\text{C}$, $m = 18$ for $^{18}\text{O}/^{16}\text{O}$, or $m = 45$ for $^{45}\text{CO}_2/^{44}\text{CO}_2$). Here, the stated reference may be VPDB, VPDB- CO_2 , NBS19- CO_2 , VSMOW- CO_2 , or the WRG. Since a delta value is normally a highly precise value between -0.1 and $+0.1$, it is commonly multiplied by 1000 and denoted by ‰ (*per mill*).

$$\delta_{\text{sample/reference}}^m = \left[\frac{{}^m R_{\text{sam}} - {}^m R_{\text{ref}}}{{}^m R_{\text{ref}}} \right] \quad \text{Eq. 1}$$

- α . The symbol *alpha*. A dimensionless quantity, known as the fractionation factor, is used to express the fractionation expected from isotopic exchange between two substances under standard conditions. For example, the fractionation in $^{18}\text{O}/^{16}\text{O}$ expected when CO_2 is equilibrated with H_2O is expressed in Eq. 2, where ^{18}R values are $^{18}\text{O}/^{16}\text{O}$ ratios in CO_2 and H_2O . For further details, see O’Neil (1986).

$$\alpha_{\text{CO}_2-\text{H}_2\text{O}}^{18} = \frac{{}^{18}R_{\text{CO}_2}}{{}^{18}R_{\text{H}_2\text{O}}} \quad \text{Eq. 2}$$

- λ . The symbol *lambda*. A dimensionless quantity used to express the relationship between the stable isotope ratios of oxygen in a sample with that in a reference material (Eq. 3). The letter a has also been used for this purpose but we wish to avoid confusion with the symbol *alpha*. A value for λ is needed to convert $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ measurements to $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$

$$\frac{{}^{17}R_{\text{sam}}}{{}^{17}R_{\text{ref}}} = \left[\frac{{}^{18}R_{\text{sam}}}{{}^{18}R_{\text{ref}}} \right]^\lambda \quad \text{Eq. 3}$$

values, and before precise measurements of this quantity were available, 0.5 was set as the accepted value. The historical constancy of this accepted value is important for maintaining the intercomparability of past and future measurement results. However, precise measurements of the true value and natural variation in *lambda*, and the resultant influences on the accuracy and uncertainty of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, have been recent concerns of the IAEA Consultants’ Working Group on Light Stable Isotope Reference Materials.

- η . The symbol *eta*. Here, a dimensionless quantity used to express cross-contamination coefficients η_{45} and η_{46} . Values of η indicate the fraction of reference gas that contaminates the sample, and vice versa, during dual-inlet measurements. Cross-contamination is considered a property of a particular IRMS dual-inlet system during a particular time, and is dependent upon the instrumental settings under which measurements are performed.
- ω . The symbol *omega*. Here, a quantity used to express the average relative change between sample-to-sample measures of the WRG voltage ratio, which is a metric of inconsistency in ion source conditions. Values of ω are considered related to the level of uncertainty in applied values of η .

Introduction

Isotope reference materials are used to relate field measurements to stated references in many applications of economic, industrial, and global relevance. The total combined uncertainties of these field measurements are, in large part, due to uncertainties in the realization of the internationally accepted isotope ratio scales. This situation arises from the uncertainties in value assignments of Reference Materials (RMs) and, more fundamentally, lack of control of subtle physicochemical and instrumental factors that limit the accuracy and reproducibility of isotopic measurements. Because these factors can be complex combinations of many variables, intercomparison exercises across independent laboratories have been considered the best method to represent and explore the broad range of variables and to establish consensus values for RMs. In the past, participants had been asked to perform measurements of RMs, self-evaluate the data, and report "best" results (Hut 1987, Stichler 1995, Verkouteren 1999). The resulting reproducibility *among* laboratories was two-to-ten times poorer than the sample repeatability *within* the average laboratory, with variability increasing as the compositional difference increased between the RM and the realization point of the isotope ratio scale. Because total uncertainties of RM value assignments reflect the variation in intercomparison results, this problem has hindered consensus in value assignments, the intercomparability of standardized results across measurement networks, and the development of new and improved isotope measurement methods due to difficulty in benchmarking and validating performance. For example, a 0.1 ‰ variation in the determination of $\delta^{13}\text{C}$ can translate to a variation (or misallocation) of 0.2 % in the apportionment of distinct carbon sources. In terms of the atmospheric carbon inventory, this variation could translate up to one PgC (10^{15} g C), which would be the size of a regionally significant carbon source or sink.

This report summarizes the results of a special intercomparison exercise which has also produced new NIST RMs. The goal of this exercise was to improve, by at least a factor of two, the uncertainties of value assignments for a suite of light stable carbon and oxygen isotope RMs distributed by the IAEA and the NIST. This required designing a special intercomparison exercise, which was initialized by the IAEA Light Stable Isotope Advisory Working Group in 1998. Incorporated into the design were mandatory procedures (Appendix 1) involving:

1. standard conditions for the chemical derivation of CO_2 from the RMs;
2. the use of a broad array of dual-inlet IRMS systems with triple collectors;
3. a specified sequence of replicated analyses to be performed within 24 hours (if possible) against a single Working Reference Gas (WRG). The sequence was selected to minimize the compositional differences between samples, thereby minimizing sample-to-sample memory effects;
4. the fixed setting of instrumental parameters and CO_2 inlet pressures during the analysis sequence;
5. the reporting of raw voltage ratios as well as $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ measurements;
6. the direct measurement of the "cross-contamination" effect (Meijer et al., 2000) within each IRMS instrument during the analysis sequence, and;
7. the return of a questionnaire detailing laboratory discretionary procedures and the values of unrestricted variables.

Nine laboratories with internationally recognized expertise were invited to participate. The Standard Reference Materials Group (SRMG) of NIST provided the participants with units of the Reference Materials, while the Centrum voor IsotopenOnderzoek (CIO) Rijksuniversiteit Groningen provided isotopically enhanced samples of pure CO₂ (GS-40). Additionally, intercalibrated hydrometers were included for specific gravity measurement of the phosphoric acid used for the carbonate digestions. The eight laboratories that reported data are listed in Table 1, while the suite of analyzed materials is listed in Table 2.

Laboratory Performance Metrics

The requirement for reporting raw $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ data (against the working machine gas) instead of reporting $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values served to avoid biases from prior knowledge of value assignments.² This precaution, combined with centralized data processing (Verkouteren and Lee, 2001) circumvented potential inconsistencies among data reduction algorithms and outlier rejection procedures.

NIST received measurement data from each laboratory in electronic form (Appendix 2). Data were merged into a spreadsheet and quality control checks were performed to identify and, with the help of the participants, correct data inconsistencies. The basic 8-laboratory dataset (as an Excel file) is available at <http://www.cstl.nist.gov/div837/837.01/outputs/NIMICONI.xls>. Lab#8 had severe instrumental difficulties and was unable to run the specified analytical sequence of 49 samples. We have included their incomplete data here for comparison purposes, but have not used the data in the statistical evaluations beyond Figure 1. The remaining dataset consisted of 343 sample runs of which 16 were missing due to lost samples.

After the data were validated, we compared $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ measurement repeatability within the laboratories for each RM (Figure 1). The medians of the average repeatability (standard deviation) of $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ measurements for each sample type were: 0.022 ‰ and 0.068 ‰ (waters); 0.033 ‰ and 0.049 ‰ (carbonates); 0.015 ‰ and 0.012 ‰ (carbon dioxides).

We plotted measured voltage ratios for the WRG across the entire analytical sequence (Figures 2 and 3). These ratios are very sensitive indicators of the stability of conditions in each ion source. While gradual drift in these ratios is normal, abrupt shifts suggest that inlet pressures or ion source settings may have changed, or that the measurements were taken over extended periods. Under these circumstances, the degree of cross-contamination across the measurement sequence would also change, compromising our ability to correct for this effect. The average relative change between successive measures of a voltage ratio represents the degree of inconsistency in ion source conditions, represented by ω (Eq. 4), where Z is the voltage ratio of m/z 45 to m/z 44 ($n = 45$) or m/z 46 to m/z 44 ($n = 46$), x is the total number of sample runs in the measurement sequence (here, $x = 43$ for the full pre-GS-40 sequence), and i is the run number. The ω values for each laboratory are listed on the plots in Figures 2 and 3, as well as in Table 3. Values for

$$\omega^n = \frac{10^6}{x-1} \sum_{i=2}^x \frac{|Z_i^n - Z_{i-1}^n|}{Z_i^n} \quad \text{Eq. 4}$$

² Long-recognized is the “SRM Syndrome” (Byrne 1974), where analysts can succeed in repeating reported results, but fail when such samples are presented as blind unknowns.

Lab#7 were significantly higher than the other laboratories, and Lab#8 reported no voltage ratio data. It is reasonable to assume that the values of ω are proportional to the uncertainty of the cross-contamination coefficient, although the explicit relationship has not been determined. For now, we report the calculated values of ω to indicate relative instability in the voltage ratios and increased uncertainty in the cross-contamination correction, but do not use ω to exclude data.

In Tables 4A and 4B, we list raw $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ measurements of the RMs versus WRG, along with standard uncertainties (u_i) based upon measurement repeatabilities. These data were then corrected for cross-contamination and standardized against the NBS19-CO₂ measurements as described in the following section. Values of standardized $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ with u_c greater than 0.2 ‰ were deemed too uncertain to include in subsequent calculations. These included all the measurements from Lab#8, all $\delta^{46}\text{CO}_2$ measurements from Lab#7, all LSVEC measurements from Lab#1, and $\delta^{46}\text{CO}_2$ SLAP measurements from Lab#2 and Lab#4. These excluded data, however, were included in the subsequent statistical evaluation of the discretionary procedures. Remaining data, consisting of 100 averaged results from 7 laboratories, were corrected for cross-contamination and processed into $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VPDB,CO}_2}$ results as described below.

Calculations

Cross-Contamination Correction

For $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ measurements in each instrument, cross-contamination correction factors (η_{45} and η_{46}) were determined by using the isotopically-enhanced GS-40 gas between repetitions of the laboratory standard gas (LSG) near the end of the analysis sequence (Figure 4, plots A and B). Mandatory procedures required that all samples be analyzed at a fixed inlet pressure and $m/z = 44$ voltage, even though the $m/z = 45$ and $m/z = 46$ pre-amplifiers might saturate when analyzing the GS-40 sample. Unfortunately, in three of the six laboratories, the inlet pressure was decreased (either manually or by automated control) to unsaturate these pre-amplifiers. This action altered gas conditions in the ion source and prevented an accurate measure of the cross-contamination effect during the analysis sequence. Later, two of these laboratories were able to rerun a shortened sequence of the gases to allow reasonable estimates of the effect, although we note that the level of cross-contamination may have shifted considerably during the delay. The values of η_{45} and η_{46} were calculated through Equation 5:

$$\eta_m = \Delta Z_{\text{WRG}}^m / (\Delta Z_{\text{WRG}}^m + \Delta Z_{\text{ES}}^m) \quad \text{Eq. 5}$$

where: m is 45 or 46, signifying the minor m/z isotopomers of the ratio considered (against the $m/z = 44$ isotopomer); ΔZ_{WRG} is the absolute difference in voltage ratio measurements of the working reference gas (introduced through inlet 2) before and during the GS-40 analysis; and ΔZ_{ES} is the absolute difference in voltage ratio measurements between GS-40 and the laboratory standard gas (introduced through inlet 1). The calculated η values were applied to correct the raw $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ values (as measured against the working reference gas) as follows (Meijer et al., 2000):

$$\delta_{\text{corr}}^m = (\delta_{\text{meas}}^m) / (1 - 2\eta_m - \eta_m \delta_{\text{meas}}^m) \quad \text{Eq. 6}$$

One laboratory (Lab#1) had no appropriate measurements of the GS-40 material. The η_{45} and η_{46} values were therefore determined through that laboratory's measurements of RM 8562 referenced to RM 8563 (Eq. 7). This required knowledge of the true differentials in the RM values, which are consistent with this exercise and verified by subsequent measurements at NIST.

$$\eta_m = \frac{\delta_{true}^m - \delta_{obs}^m}{\delta_{true}^m (2 + \delta_{obs}^m)} \quad \text{Eq. 7}$$

Standardization

Tables 5A and 5B list the cross-contamination corrected $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ measurements versus WRG. These corrected measurements were standardized against the corrected NBS19- CO_2 measurements through Eq. 8, the results of which are listed in Table 6A and 6B.

$$\delta_{sample/NBS19.CO2}^m = \frac{(\delta_{sample/WRG}^m + 1)}{(\delta_{NBS19.CO2/WRG}^m + 1)} - 1 \quad \text{Eq. 8}$$

The standardized values in Tables 6A and 6B are the primary measurement-based results of this exercise. While corrected for cross-contamination, they are entirely independent of assumptions regarding oxygen isotope relationships, fractionation constants, and the definition of the VPDB scale. After this point, assumptions were applied to relate these measurements to the VPDB- CO_2 scale, to convert the measurements to $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, and to correct the VSMOW and SLAP results for gas dilution effects.

Conversion

The standardized measurements were related to the VPDB scale through Eq. 9, where $\delta_{NBS19.CO2/VPDB.CO2}^{45}$ and $\delta_{NBS19.CO2/VPDB.CO2}^{46}$ are defined as +1.75637 ‰ and -2.19377 ‰, respectively (Allison, Francey and Meijer 1995). Values of $\delta^{13}\text{C}_{VPDB}$ and $\delta^{18}\text{O}_{VPDB.CO2}$ were then

$$\delta_{sample/VPDB.CO2}^m = (\delta_{sample/NBS19.CO2}^m + 1) (\delta_{NBS19.CO2/VPDB.CO2}^m + 1) - 1 \quad \text{Eq. 9}$$

calculated through the internationally accepted algorithm, which was facilitated through a Web-based data processing tool (Verkouteren and Lee, 2001). Implicit in the definitions of $\delta_{NBS19.CO2/VPDB.CO2}^m$ and the IAEA algorithm were several assumptions that were applied consistently. These included the following:

- $\delta^{13}\text{C}$ (NBS19 vs VPDB) = 1.95 ‰ exactly
- $\delta^{18}\text{O}$ (NBS19 vs VPDB) = -2.20 ‰ exactly
- $\alpha_{\text{CO}_2\text{-NBS19}}^{18} = \alpha_{\text{CO}_2\text{-VPDB}}^{18} = 1.01025$ (see Eq. 2)
- $\alpha_{\text{CO}_2\text{-VSMOW}}^{18} = \alpha_{\text{CO}_2\text{-SLAP}}^{18} = 1.0412$ (see Eq. 2)
- $\lambda = 0.5$ (see Eq. 3)
- $^{17}R_{\text{ref}} = 0.000378866601$, $^{18}R_{\text{ref}} = 0.002067160680$ (ref = VPDB-calcite, Allison et al., 1995)

Gas Dilution Correction

To compensate for the gas dilution effect in the water samples, the VSMOW and SLAP delta values were corrected through Eq. 10 (Craig 1957), where ρ is the mole fraction of water to CO_2 used in the isotope exchange, α is the isotope fractionation factor for oxygen-18 between CO_2 and H_2O at the temperature utilized (Brenninkmeijer et al., 1983), and $\delta^{18}\text{O}(\text{gas})$ is the original delta value of the CO_2 gas used in the exchange. For VSMOW, this correction ranged from 0.01 ‰ to 0.06 ‰ (ρ values from 920 to 185) except for Lab#4 where the correction was 1.09 ‰ ($\rho = 15$). For SLAP, the correction amounted to -0.03 ‰ to -0.25 ‰ except for Lab#4 (-2.53 ‰).

$$\delta^{18}\text{O}(\text{corr}) = \left[1 + \frac{\alpha}{\rho}\right] \delta^{18}\text{O} - \left[\frac{\alpha}{\rho}\right] \delta^{18}\text{O}(\text{gas}) \quad \text{Eq. 10}$$

Normalization

Mean $\delta^{18}\text{O}$ values for all RMs were normalized so that $\delta^{18}\text{O}_{\text{NBS19/VPDB}} = -2.2$ ‰ and $\delta^{18}\text{O}_{\text{SLAP/VSMOW}} = -55.5$ ‰ (Coplen 1988; Coplen 1996).

Unrestricted Variables

In addition to the measurement data, each laboratory completed a questionnaire regarding discretionary chemical and instrumental procedures (Appendix 3). This information was used to evaluate over 30 unrestricted variables (Table 7) that may have influenced the reproducibility of the measurements. There were three important types of unrestricted variables: reported numerical measurements and settings (CODE = R); values calculated from reported measurements (CODE = C); and interpreted procedural differences (CODE = I). For this last type, integer values were assigned based upon the differences among procedures used in each laboratory. Correlation analysis and Principal Components Analysis (PCA) were then used to explore the relationships among the unrestricted variables and the measurement results. To simplify and improve the interpretation of PCA, matrices were selected to explore cohesive subsets of the variables and results.

Results and Discussion

Table 8 presents a summary of results from the intercomparison, along with recommended value assignments and comparisons to previous reference values. Appendix 4 contains individual laboratory results calculated through four different sets of assumptions.

Outliers

Among the 100 standardized RM results, there was a single 2-sigma outlier ($\delta^{18}\text{O}$ of VSMOW, Lab#4); this outlier had a procedural explanation (see discussion of **Effects from Unrestricted Variables - Water Samples**, p.13-14). The scarcity of outliers can be attributed, in part, to the expertise of our selected participants, and to the pre-exclusion of data based on instrument performance standards. By comparison, the Stichler (1995) exercise, an intercomparison that included many of these materials, reported 139 results (plus 15 missing values). In this earlier exercise, eleven of the reported results were identified as 2-sigma outliers, with another six flagged in sequential 2-sigma determinations. That study was designed partially as a learning exercise, where participation was open and a greater range of expertise was represented. However, the resulting dispersion of the results created difficulties in data evaluation. Without performance standards it is difficult to justify the exclusion of outliers, yet, the consequence of

including them are uncertainty bounds that prevent precise value assignments. The scarcity of outliers was therefore an important benefit of our exercise.

Cross-Contamination Coefficient

In this exercise, the determinations of the η_{45} and η_{46} values were not completely straightforward. Inspection of plots in Figures 2 and 3 show that the perturbations to the WRG voltage ratios from the repeated GS-40 analyses (Run Sequence 44-46) frequently exhibited an *approach* to a new equilibrium. This suggests that source gas loading and outgassing behavior (hence the cross-contamination effect) had a time component much greater than the dual inlet switchover idletime (Verkouteren et al., 2003a). This complicated the cross-memory determination, so we used those replicated measurements that were closest to the new equilibrium and which maximized the ΔZ_{WRG} and η values; relative uncertainty of the η values is estimated at 30%. Comparison of η_{45} and η_{46} values, calculated for all laboratories using the GS-40 and RM methods, also shows some discrepancies. Some η values determined by the RM method are negative, which may arise as artifacts from measurement uncertainty, but also may suggest that the cross-contamination model only partially explains the dispersion in the data. This deserves further investigation. For now, we consider the GS-40 results as the best estimation of the cross-contamination effect. The cross-contamination coefficients determined for each instrument are listed in Table 3. Generally $2 \cdot \eta_{45} \approx \eta_{46}$, although there are exceptions: in Lab#4 the values are comparable, while in Lab#5 the η_{46} value exceeded η_{45} by about a factor of nine. This could reflect high water levels in the leaks or ion source, which could increase the cross-memory of m/z 46 preferentially. Lab#5 reported that their source had not been cleaned for two years, which may have contributed to the observed behavior.

Results

Cross-contamination corrections ranged from -0.01 ‰ to -0.33 ‰ among results from individual laboratories. Corrections to the averaged results were very consistent, amounting to $0.0018/\Delta^{13}\delta$ and $0.0035/\Delta^{18}\delta$ where $\Delta\delta$ was the difference between the delta values of the sample and NBS19-CO₂. These averaged corrections ranged from -0.00 ‰ to -0.20 ‰. In every case, the corrected $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values were more negative than the previously accepted reference values (included in Table 8 for comparison purposes). While a negative shift was expected from the correction for cross-contamination, this factor was only partially responsible for the total corrections. We cannot attribute the remainder of the shifts to any specific factor, but are confident that some combination of the specific chemical and instrumental protocols and centralized data processing was responsible.

Average corrected $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values and standard uncertainties are given in columns six and seven of Table 8. The mean $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values from this exercise are well within the 2-sigma bands of the previous reference values. Generally, the uncertainties of the new $\delta^{13}\text{C}$ values are much improved (in some cases reduced by over a factor of two) over the previous uncertainties. Recommended values (column eight of Table 8) for $\delta^{13}\text{C}$ are essentially identical with the intercomparison results, whereas for $\delta^{18}\text{O}$ we have normalized the results so that $\delta^{18}\text{O}_{\text{NBS19/VPDB}} = -2.2$ ‰ and $\delta^{18}\text{O}_{\text{SLAP/VSMOW}} = -55.5$ ‰ (Coplen 1996). The combined standard uncertainties (u_c) for the recommended values arise from the reproducibility of the intercomparison results and, for $\delta^{18}\text{O}$, the uncertainty in the normalization procedure. The $\delta^{13}\text{C}$ assignments of the CO₂ RMs remain essentially unchanged from the prior determination (Verkouteren, 1999).

Other Comparisons

Comparison of the CO₂ RM value assignments with those proposed through Meijer et al. (2000) deserves comment. Those proposed values, based on the measurement data from the 1997 intercomparison (Verkouteren, 1999), were generated under the assumption that the observed dispersion in the data was due entirely to the varying contributions of cross-contamination in each analyzing instrument. This cross-contamination model (CCM) predicted values, especially for the materials isotopically depleted against NBS19-CO₂, which were beyond the most negative values collected in the 1997 exercise. While we had recognized that a consensus mean would not be an accurate assignment for any of these materials, our measurements of the *difference* in compositions *among* the CO₂ RMs using self-consistent $\delta^{45}\text{CO}_2$, $\delta^{46}\text{CO}_2$, and $\delta^{47}\text{CO}_2$ measurements supported only modest corrections in the consensus means. In part, this current exercise was designed to resolve the discrepancy.

Here, we have found that the prior assignments for $\delta^{13}\text{C}$ in the CO₂ RMs have been justified, with minor adjustments within the original uncertainty bounds. All values for $\delta^{18}\text{O}$ have been shifted by about -0.1 ‰, due mainly to an improved realization of the VPDB oxygen-18 scale. The new value assignments are now based upon consensus means that consider the contributions from cross-contamination. We believe that the CCM, which was a reasonable attempt at improving value assignments, was limited by its application to our data from the 1997 intercomparison. These data were "best results" of measurements made at each participating laboratory, where no information was collected regarding the variation in ion source conditions or time needed to complete the measurements. As such, it is extremely unlikely that fixed cross-contamination coefficients could be applied accurately to all data reported from any laboratory. Secondly, there were unverifiable factors other than cross-contamination, such as the balance and control of fractionation between the leaks, preparation of NBS19-CO₂, and data reduction, which could lead to scale shifts or expansion rather than the simple scale contraction assumed in the CCM. The uncertainties expressed from the application of this model were based on the fit of the data, but were not comprehensive in the evaluation of other potential contributions.

Effects from Unrestricted Variables

Visual inspection, correlation analysis, and multivariate evaluation of relationships between the discretionary variables and the standardized (and unnormalized) results – both corrected and uncorrected for cross-contamination – were performed to identify and explore possible factors of significance. While these evaluations were severely limited by the large number ($N > 30$) of unrestricted variables and the small number ($N = 7$) of reporting laboratories, some patterns were evident. Effects on water samples (VSMOW, SLAP), carbonate samples (NBS-18, LSVEC, IAEA-CO-9), and CO₂ samples (RM 8562, RM 8563, RM 8564) will be discussed in turn.

Water Samples. Results for VSMOW and SLAP exhibited the largest and most interpretable dispersions. The amounts of CO₂ and water used in the isotope exchange process, as well as the amount of time allowed for isotope exchange, were determining variables. We have plotted all water data in the two plots of Figure 5, including those data earlier excluded on the basis of performance standards. Dashed lines denote accepted values. Error bars indicate standard uncertainties of the $\delta^{18}\text{O}$ results, but do not include influences from unrestricted variables.

Plot A of Figure 5 shows VSMOW-CO₂ results referenced to VPDB-CO₂, along with water-CO₂ exchange time (abscissa) and amount of CO₂ used (proportional to shaded bubble size). Data in this plot indicate the degree of closure attained between the VPDB and VSMOW oxygen-18 scales. The one outlier in the exercise (result of Lab#4) is characterized at extremes of CO₂

amount (10.9 mmol) and exchange time (4 hours). This amount of CO₂ is more than 30 times the level of the next largest amount, and the exchange time is 11 hours shorter than the next smallest time. The results from Lab#2 and Lab#7 were characterized at the lower extreme of CO₂ amount, and both values were biased from the accepted value by 0.3 ‰ to 0.4 ‰. The remaining results (Lab#1, Lab#3, Lab#5, Lab#6) precisely clustered on the accepted value, and were similar in the amounts of CO₂ and times used in the isotopic exchange.

Plot B of Figure 5 shows SLAP-CO₂ results referenced to VSMOW-CO₂ (these are the only results reported in this report that are independent of the NBS19-CO₂ measurements). Data in this plot test consistency with the IUPAC-accepted value of $\delta^{18}\text{O SLAP} = -55.5 \text{ ‰}$ used to define the VSMOW/SLAP normalized scale. Water-CO₂ exchange time is plotted along the abscissa, with unshaded bubble size proportional to the reported H₂O/CO₂ molar ratio. Results of three labs (Lab#2, Lab#4, Lab#7) had been excluded by the performance standard of repeatability ($u_c > 0.2 \text{ ‰}$) but are included here. Of these, only the imprecise Lab#4 and Lab#7 results were statistically consistent with the IUPAC value. In contrast, the precise cluster of results from Lab#1, Lab#3, and Lab#5 give a $\delta^{18}\text{O SLAP}$ value of -56.18 ‰ ($u_i = 0.01 \text{ ‰}$), which is also supported by the (excluded) result of Lab#2.

The relatively short times (5 h) used for H₂O-CO₂ isotopic exchange in Lab#4 may have influenced $\delta^{18}\text{O}$ values and repeatability. After 16 h at 25 °C with agitation, equilibration is indicated by the consistency of the Lab#1-Lab#3-Lab#5 cluster. We note that while Lab#6 used a 25 h exchange time at 25 °C, they did not agitate the H₂O-CO₂ mix. This lack of agitation may be significant: Lab#2, which used amounts of water similar to Lab#6 and no agitation, achieved a $\delta^{18}\text{O}$ value consistent with the Lab#1-Lab#3-Lab#5 cluster after 48 hours.

The difference between the accepted value of $\delta^{18}\text{O SLAP}$ and that determined by the Lab#1-Lab#3-Lab#5 cluster is -0.68 ‰ , and cannot be explained simply by the correction from cross-contamination, the average of which was -0.20 ‰ . With the precise result of Lab#6 averaged into the cluster, the mean becomes -56.07 ‰ ($u_i = 0.22 \text{ ‰}$), which still is significantly different (at the 95% level of confidence) from the accepted value of -55.5 ‰ . Results suggest that the true value for $\delta^{18}\text{O SLAP}$ vs VSMOW lies between -55.7 ‰ and -56.2 ‰ . The averaged water results in Table 8 include Lab#6, but we recommend that future intercomparison exercises specify that exchange times be greater than 16 hours and that agitation be utilized.

Carbonate Samples. The repeatability of carbonate $\delta^{45}\text{CO}_2$ measurements was strongly correlated with sample size, although the correlation disappeared for $\delta^{46}\text{CO}_2$ measurements. This is illustrated in Figure 6 for NBS19-CO₂ measurements against WRG. Since the VPDB scale is directly realized through measurements of NBS19-CO₂, this link in the traceability chain affects the combined uncertainty of all $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ results. Our results suggest that using carbonate sample sizes of at least 20 mg would minimize uncertainty in $\delta^{13}\text{C}$.

A specific question for the exercise was to determine whether the range in specific gravity of the various phosphoric acids would affect the $\delta^{18}\text{O}$ results. Through reported measurements in the distributed hydrometers, specific gravity of the phosphoric acids ranged from 1.89 to 1.94, corresponding to 102.3 to 106.5 “%H₃PO₄” (Wachter and Hayes, 1985). In Figure 7, we plot the $\delta^{18}\text{O}$ values of RM 8562 and NBS-18-CO₂ against the specific gravity of the acid. We include the non-carbonate RM 8562 since all results are standardized against CO₂ generated from NBS19 carbonate digestion. A specific gravity effect may therefore not appear in carbonates but may manifest itself in non-carbonates. However, no significant correlations were apparent for

any of the samples and we conclude that the range of phosphoric acid compositions did not influence the results.

Results of NBS-18-CO₂, IAEA-CO9-CO₂, and LSVEC-CO₂ exhibited moderate interlaboratory variation (combined standard uncertainties of 0.03 ‰ to 0.19 ‰ and 0.07 ‰ to 0.21 ‰ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively). We wished to identify factors most responsible for this variation. For this purpose, we performed PCA on a data matrix consisting of the unrestricted variables under the categories of “Phosphoric Acid” and “Acid/Carbonate Reaction” (Table 7), and against each of the dependent variables ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ results for NBS-18-CO₂, IAEA-CO9-CO₂, and LSVEC-CO₂). Our strategy was to look for consistently high correlations between the principal components (eigenvectors) and each candidate response variable, then identify the variables of highest loading (or weights) in these eigenvectors that had the largest explanatory power for response.

While the PCA results for each material indicated a particular pattern of influencing variables, these patterns were only moderately consistent across the carbonate materials and did not point to any one factor as being of major significance. For example, variations in LSVEC and IAEA-CO-9 results, which are similar in $\delta^{13}\text{C}$ value, were nearly equally influenced by sample size, amount of acid used, the volume of the reaction vessel, and the duration of the reaction, contrasted with the specific density of the acid. On the other hand, the $\delta^{13}\text{C}$ results of NBS-18 were influenced more heavily by the amount of acid, and contrasted with the sample size and volume of reaction vessel. Of possible interest was the observation that the specific density of the acid had a marginally stronger influence on $\delta^{13}\text{C}$ results uncorrected for cross-contamination.

PCA on the $\delta^{18}\text{O}$ results for the carbonates exhibited a large level of randomness. We draw the conclusion that no particular unrestricted variable was important to the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ results of the carbonates in this study. This is quite plausible given that all carbonate results were standardized to the NBS19-CO₂ results, so carbonate-specific factors could have been diminished.

The normalized (and assigned) $\delta^{18}\text{O}$ value of NBS18 is -23.01 ‰, which compares favorably to -23.00 ‰, the value determined by Coplen, Kendall and Hopple (1983) through the same normalization procedures. The normalization, however, adds significant uncertainty to all assigned $\delta^{18}\text{O}$ values, since these were dependent upon the less precise measurements of the VSMOW and SLAP waters.

CO₂ Samples. RM 8562, RM 8563, RM 8564, and LSG were generally the most repeatable and most reproducible samples, an observation anticipated from the absence of chemical processing. Results of these materials were useful for exploring the variables of the measurement process. First, we investigated suspected bivariate relationships by plotting the most variable $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ results (RM 8563) against the composition of the WRG (Figure 8) and against instrument sample-reference switchover time (Figure 9). Also in Figure 9, we plotted results corrected and uncorrected for cross-contamination. No obvious dependencies were evident. The corrected results were marginally less variable than the uncorrected results, and the cross-contamination effect and variability seemed to be a minor component of the total variability. We had anticipated otherwise. Another factor seemed to be responsible for the observed variability.

We investigated all “Inlet” and “Measurement” variables in Table 7 using PCA as detailed in the section on Carbonate Samples. We compared the corrected and uncorrected results for RM 8563, which exhibited the greatest variation. This PCA analysis indicated that uncorrected $\delta^{13}\text{C}$ and

$\delta^{18}\text{O}$ results exhibited strong negative correlations with eigenvectors heavily weighted by combinations of “time” variables (evacuation time, idle time, and integration time) and exhibited positive correlations with acceleration voltage. These correlations essentially disappeared in the corrected dataset. These observations are explained below.

In some instruments, higher accelerating voltages are used to increase m/z resolution and sensitivity. However, accelerating voltage is also known to influence the amount of ion-induced sputtering in an ion source, which augments cross-contamination and sample-to-sample memory. In this exercise, we corrected for the cross-contamination that acted across the sample-reference gas switchover times (idle time plus integration time). Indeed, the dependencies noted in the variation of RM 8563 results with accelerating voltage and measurement times disappeared when cross-contamination was taken into account.

There remains our attempt to explain the observed variation in the corrected RM results. PCA suggests that single eigenvectors (i.e., factors) explained more than 80% of the variation. For $\delta^{13}\text{C}$, the instrument model appeared to be the most important factor; for $\delta^{18}\text{O}$, the three “time” variables mentioned above were most important, followed closely by the specific gravity of the phosphoric acid used to prepare the NBS19- CO_2 used for standardization. While these results are suggestive, they are not compelling since variables of measurement would be expected to act fairly consistently across all materials and delta values. This consistency was not observed so we judged that the PCA was inherently limited by the small variation in results, the small number of laboratories, and the large number of variables. We also consider that the major source of the variation was either not considered in our set of unrestricted variables, or that the metrics used were inadequate to accurately characterize the influential factor.

IRMS instruments are dynamic systems where the levels and compositions of background are constantly changing. The specific method each laboratory used to measure and compensate for the changing background was discretionary, but we did not collect detailed information on this factor. Future exercises should consider this potentially significant factor more carefully.

Memory and conditioning effects in IRMS systems can have half-lives of a few minutes (Verkouteren et al., 2003a), which are not fully compensated by corrections for short-term cross-contamination or long-term background. We attempted to control these mid-term effects through the experimental design, which included a specified analysis sequence with replication ($n = 2$ to 5) and short total duration (24 hours if possible). We were only partially successful in compensating for mid-term effects, which cause delta measurements to be influenced by the composition of the prior sample; this was noted frequently in the exercise. We also noted that the observed voltage ratios of the WRG tended to drift in one direction during the analysis sequence, and to shift during breaks in that sequence. These breaks could be short, such as extended evacuations between certain samples, or longer due to practical considerations by the analyst. In any case, there were inherent limitations in our attempt to control ion source conditions during the entire analytical sequence, which was needed to optimize the standardization procedure and to enable a representative measurement of cross-contamination. This limitation may have played a role in the observed variation of sample results. The performance metric ω was formulated to measure this limitation across the analysis sequence.

NIST Measurements

By measuring $\delta^{47}\text{CO}_2$ along with $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$, measurement accuracy may be tested. The *measured* $\delta^{47}\text{CO}_2$ value will be identical statistically to the *expected* $\delta^{47}\text{CO}_2$ value (as calculated from $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$) when all three measurements are accurate, a condition difficult to satisfy in the presence of cross-contamination. Accurate measurements, as verified by this technique, became possible only after improvements were made to the ion source of the NIST instrument (Verkouteren et al., 2003b). Additionally, an idletime of at least 60 seconds and a fully opened Variable Ion Source Conductance (VISC) window were necessary to eliminate significant sample-reference cross-contamination. The detector array was configured for measurement of the m/z 44, 45, 46, and 47 ion beams, using resistors of 30 M Ω , 3 G Ω , 10 G Ω , and 1 T Ω , respectively. About 28 kPa of inlet pressure was needed to generate a 4 volt (or greater) signal across each resistor. Operating pressure in the ion source was about 50 μPa and instrument response was linear up to this level. The precision limit (standard uncertainty) due to shot noise (Merritt and Hayes, 1994) was 0.004 ‰, 0.006 ‰, and 0.056 ‰, for $\delta^{45}\text{CO}_2$, $\delta^{46}\text{CO}_2$, and $\delta^{47}\text{CO}_2$ respectively, which was closely approached in measurement repeatability. Since the ThermoFinnigan³ MAT 252 signal acquisition system (ISODAT version 6.1) was configurable to measure only three beams (two ratios) simultaneously, methods were used that alternated repeatedly between two detector configurations: [$\delta^{45}\text{CO}_2 + \delta^{46}\text{CO}_2$] and [$\delta^{45}\text{CO}_2 + \delta^{47}\text{CO}_2$].

Replicated measurements of $\delta^{45}\text{CO}_2$, $\delta^{46}\text{CO}_2$, and $\delta^{47}\text{CO}_2$ among three laboratory standard gases (LSG) and the three RMs are listed in Table 9. The $\delta^{47}\text{CO}_2$ value expected from accurate measurement of $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ was calculated by numerical methods and compared to the observed value. In all cases, the calculated $\delta^{47}\text{CO}_2$ values were statistically equal to the measured values, verifying the accuracy of the measurements. The $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ values (and uncertainties) between the RMs were calculated through Eq. 11, where $m = 45$ or 46 , $x = 3$ or 4 , and $y = 2$.

$$\delta_{RM\ 856x\ vs.\ RM\ 856y}^m = \left[\frac{(\delta_{RM\ 856x\ vs.\ LSGx}^m + 1) \cdot (\delta_{LSGx\ vs.\ LSGy}^m + 1)}{(\delta_{RM\ 856y\ vs.\ LSGy}^m + 1) \cdot (\delta_{LSGy\ vs.\ LSGy}^m + 1)} - 1 \right] \quad \text{Eq. 11}$$

With the compositional differences ($\Delta\delta$) among the three RMs accurately characterized, realization of the VPDB scale was made through the intercomparison results using RM 8562 (for $\delta^{13}\text{C}_{\text{VPDB}}$) and RM 8564 (for $\delta^{18}\text{O}_{\text{VPDB,CO}_2}$). These RMs exhibit the best interlaboratory reproducibility, and are closest in composition to NBS 19 CO_2 , the primary reference material. For $\delta^{13}\text{C}_{\text{VPDB}}$ in RM 8562, the value of -3.76 ‰ was assigned. This value was considered the best estimate of the true value because: 1) it represents the consensus mean of $\delta^{13}\text{C}_{\text{VPDB}}$ values corrected for cross-contamination, and 2) this value was identical to the value determined through another intercomparison exercise (Verkouteren 1999). For $\delta^{18}\text{O}_{\text{VPDB,CO}_2}$ in RM 8564, the value of -10.06 ‰ was used because: 1) this represents the consensus mean of $\delta^{18}\text{C}_{\text{VPDB,CO}_2}$ values corrected for cross-contamination, and 2) this value is consistent within the uncertainty of

³ Certain commercial equipment, instruments, and materials are identified in this paper 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.

the value previously assigned through the original intercomparison exercise (Verkouteren 1999). Through these assignments and the NIST $\Delta\delta$ measurements, the values of the remaining delta values were thereby determined; these are listed in Table 8. The combined standard uncertainty (u_c) of each assignment includes the uncertainty (standard deviation) in the defining RM, the standard deviation of the $\Delta\delta^{45}\text{CO}_2$ and $\Delta\delta^{46}\text{CO}_2$ measurements, the known sample-to-sample isotopic variation combined in quadrature, and for $\delta^{18}\text{O}$ values, the uncertainty of the VSMOW/SLAP scale used for normalization. *In all cases, the value assignments of the CO₂ RMs are within the uncertainty of results reported in the prior and current intercomparisons. As a result, all recommended value assignments may be considered consensus values, with $\delta^{13}\text{C}$ uncertainties improved by the NIST measurements.*

Algorithm Considerations

Appendix 4 contains individual laboratory results calculated from measurement data in Table 6 using four different sets of fundamental assumptions regarding oxygen isotopes. Besides measurement data, an algorithm must fix two independent variables, λ and $^{17}\text{R}_{\text{ref}}$ (see Eq. 3). These may be recast into two interdependent variables λ and K , where $K = ^{17}\text{R}_{\text{ref}}/(^{18}\text{R}_{\text{ref}})^\lambda$ and $^{18}\text{R}_{\text{ref}}$ is usually taken from Baertschi (1976) for VSMOW or Allison et al. (1995) for VPDB.

Table 10-A (in Appendix 4) contains results using the IAEA-recommended values of $\lambda=0.5$ and $K=0.0083330$ (Assumption Set A). As results of this intercomparison are the most precise to date, they directly expose the well-known problem of interdependence of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values calculated using these assumptions, and exhibited in the $\delta^{13}\text{C}$ values of VSMOW-CO₂, SLAP-CO₂, and LSG. These values should be identical within any laboratory, but differences of 0.1 ‰ to 0.3 ‰ are the result in this exercise. This long-standing issue has been tolerated to preserve long-term historical intercomparability of $\delta^{13}\text{C}$ values in the literature, and this is a valid reason to continue the practice. However, we also note that use of this set of assumptions compromises the ability to use ^{13}C as a conservative tracer in high-precision applications, such as in atmospheric chemistry and forensic studies, since $\delta^{13}\text{C}$ values calculated through Assumption Set A are influenced by the oxygen composition of the CO₂. This is also an intercomparability issue, and a concern with CO₂ samples collected across latitudes and altitudes where oxygen isotopic compositions are highly variable, and in laboratory settings where carbonaceous materials are combusted with oxidants having different oxygen compositions.

We recalculated $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values using other assumption sets. In Appendix 4, Table 10-B uses $\lambda = 0.516$ (Matsuhisa et al., 1978) and $^{17}\text{R}_{\text{VSMOW}} = 0.0003799$ (Li et al., 1988). Table 10-C uses $\lambda = 0.516$ and $^{17}\text{R}_{\text{VSMOW}} = 0.000402326$ (Santrock et al., 1985), and Table 11-D uses $\lambda=0.528$ (Meijer and Li, 1998) and $^{17}\text{R}_{\text{VSMOW}} = 0.000386913$ (Assonov and Brenninkmiej, 2002). In each table, the degree of similarity of the $\delta^{13}\text{C}$ values for VSMOW-CO₂, SLAP-CO₂, and LSG in each laboratory is determined by two simple methods: 1) The difference between $\delta^{13}\text{C}_{\text{VPDB}}(\text{VSMOW-CO}_2)$ and $\delta^{13}\text{C}_{\text{VPDB}}(\text{SLAP-CO}_2)$ (= Fit Coeff.1), and 2) standard deviation of the mean of $\delta^{13}\text{C}_{\text{VPDB}}(\text{VSMOW-CO}_2)$, $\delta^{13}\text{C}_{\text{VPDB}}(\text{SLAP-CO}_2)$, and $\delta^{13}\text{C}_{\text{VPDB}}(\text{LSG})$ (= Fit Coeff.2). We then pooled results that passed the measurement performance criteria for these data (from Lab#1, Lab#3, Lab#5, and Lab#6). We added the Fit Coeff.1 values, and averaged the Fit Coeff.2 values. Pooled Fit Coefficients approaching zero indicated the set of assumptions that minimized the co-variance of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values across the laboratories.

From inspection of the fit coefficients, one fact is clear: the assumption set that is currently recommended by the IAEA leads to significant and systematic co-variance of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. This co-variance can be reduced by applying other assumption sets. Assumption Set D is marginally better than the other sets, and while inconsistencies exist in individual laboratories, these tend to average out across the participants.

Conclusions

Through this exercise, we have made tangible progress in understanding and controlling the fundamental factors that influence the accuracy and reproducibility of high-precision isotope ratio measurements, and have improved the value assignments of Reference Materials used to standardize isotope measurements for many applications. This accomplishment was made possible through the commitment of many individuals and organizations in a designed exercise having strict sample preparation and measurement protocols, and where IRMS performance criteria were used to filter data. This was the first exercise to take raw measurement data from the participants and centrally process this data into standardized results. This was also the first exercise to correct for cross-contamination. For most of the materials, value assignments were shifted in part due to the cross-contamination correction, with uncertainties improved by factors up to two over the previous assignments. When the oxygen data were normalized, results were consistent with prior determinations.

In order to explain the observed variation among standardized delta values, statistical approaches were used to discern relationships between the unnormalized results and the reported values of unrestricted variables. For VSMOW and SLAP, the relative amounts of CO_2 and H_2O , exchange time, and presence of agitation during the isotope exchange process were found to relate with the variation in the $\delta^{18}\text{O}$ values. For the carbonate and CO_2 RMs, however, we show that no monitored variables were responsible for the variation observed across the RMs. While this is most likely a result of the small number of laboratories, the small variation in results, and the large number of unrestricted variables, we also consider that latent factors may be responsible. One possibility is mid-term memory that is difficult to model and correct. Subtle effects from differences in background corrections could also be present.

Lastly, we showed that the oxygen isotope assumptions in the algorithm used to convert $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ measurements to $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values could lead to interesting inconsistencies in the results of this exercise. Four assumption sets were tested, where the currently-accepted set led to the greatest inconsistencies. Another set minimized the inconsistencies across the data of this exercise, but still led to small inconsistencies within individual laboratory results.

Recommendations

1. To minimize uncertainty in the realization of the VPDB scale, samples of NBS19 carbonate should be greater than 20 mg and the amount of phosphoric acid should be at least 2 mL. The specific gravity of the phosphoric acid should be greater than 1.89 and the digestions last 6 h to 24 h at temperatures between 20 °C and 25 °C.
2. For water-RMs, we recommend that at least 1 mL H_2O be equilibrated with an amount of CO_2 where the $\text{H}_2\text{O}/\text{CO}_2$ molar ratio is greater than 200. Agitation for at least 16 hours at 25 °C should be allowed for each equilibration. Under these conditions, we recommend that

future exercises revisit the composition of SLAP vs VSMOW, and include other relevant samples such as RM 8536 (GISP: Greenland Ice Sheet Precipitation).

3. The value assignments reported here are based upon $R_{13_{VPDB}} = 0.0112372000$, $R_{18_{VPDB.CO2}} = 0.0020883491$, and $\lambda = 0.5$. Should other values become internationally accepted, then the value assignments of the RMs must be recalculated (from data in Tables 6A and 6B; see Appendix 4) to remain consistent with these definitions. Debate of issues relevant to this change is recommended. Towards making informed decisions, efforts should be made to enable and preserve intercomparability of literature values with isotope ratio scales (e.g., through conversion expressions, co-reporting results, explicit traceability, etc).
4. Reported $\delta^{18}\text{O}$ values should be normalized on an isotope ratio scale that is anchored by VPDB (where $\delta^{18}\text{O}_{VPDB}$ of NBS19 $\equiv -2.2$ ‰) and where $\delta^{18}\text{O}_{SLAP/VSMOW} \equiv -55.5$ ‰ (Coplen 1996). Note that on such a scale, the normalized $\delta^{18}\text{O}_{VSMOW}$ values of VSMOW and SLAP are not necessarily equal to 0 ‰ and -55.5 ‰, respectively.
5. The design of future intercomparison exercises of light stable isotope RMs should consider:
 - reporting raw measurements as well as best results.
 - reporting the method for background measurement and subtraction.
 - centralized data processing for consistent standardization, conversion, and data filtration based on accepted standards and performance criteria.
 - correction for cross-contamination using isotopically enhanced or depleted materials. The composition should be set so that the signals from the Faraday cups do not become saturated under the gas inlet conditions.
 - collection of information on chemical and instrumental variables and the use of multivariate methods to link variation of results with specific factors.
 - analyzing a sequence of materials by dual-inlet IRMS that would include RMs designed for GC-IRMS and EA-IRMS, such as RM 8567 (caffeine), RM 8568 (KNO_3 – low ^{18}O), RM 8569 (NaNO_3 – high ^{17}O and ^{18}O), RM 8573 (L-glutamic acid – normal ^{13}C and ^{15}N), and RM 8574 (L-glutamic acid – high ^{13}C and ^{15}N).

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Table 1. Participants of the NIST-IAEA Measurement Intercomparison for Stable Carbon/Oxygen Isotope Ratio Measurements

Laboratory	Personnel
National Hydrology Research Institute Environment Canada Saskatoon, Saskatchewan, CANADA	Len Wassenaar and Geoff Koehler
Isotope Hydrology Laboratory International Atomic Energy Agency Vienna, AUSTRIA	Manfred Groening, Ahmad Tanweer, Liliana Andreescu, Michael Van Duren
Laboratory of Isotope Geology Chinese Academy of Geological Sciences Beijing, CHINA	Tiping Ding, Rui-mei Bai, Jin-cheng Li
Maria Curie - Sklodowska University Lublin, POLAND	Stanislaw Halas
Centrum voor IsotopenOnderzoek (CIO) Rijksuniversiteit Groningen Groningen, THE NETHERLANDS	Harro A.J. Meijer, H.G. Jansen, J.J. Spriensma, R.E.M. Neubert
Laboratory of Stable Isotopes UFZ-Umweltforschungszentrum Leipzig-Halle Halle, GERMANY	Matthias Gehre, Petra Bluemel, Martina Neuber
Biogeochemical Laboratories Indiana University Bloomington, Indiana, USA	Arndt Schimmelmann, Germán Mora, Steve Studley
United States Geological Survey Reston, Virginia, USA	Sample preparation (USGS): Tyler Coplen, Jessica Hopple
National Institute of Standards and Technology Gaithersburg, Maryland, USA	IRMS measurements (NIST): Mike Verkouteren, Donna Klinedinst

Order of laboratories has been randomized and does not reflect laboratory numbers identified in this document.

Table 2. Materials Used in the Intercomparison Exercise

Carbonates

RM 8544 (NBS 19) Limestone
RM 8543 (NBS 18) Carbonatite
RM 8545 (LSVEC) Lithium carbonate
RM 8566* (IAEA CO-9) Barium carbonate

Waters

RM 8535 (VSMOW) Vienna Standard Mean Ocean Water
RM 8537 (SLAP) Standard Light Antarctic Precipitation

Carbon Dioxides

RM 8562 (Heavy, Paleomarine Origin)
RM 8563 (Light, Petrochemical Origin)
RM 8564 (Biogenic, Modern Biomass Origin)
GS-40 (Isotopically-Enhanced Material)
LSG (Individual Laboratory Standard Gas)

* RM 8566 is not yet distributed by the NIST

Table 3. Selected Performance Metrics

	Lost or Missing Samples [‡]	WRG Signal Instability		Cross-Contamination: GS-40 Method		Cross-Contamination: RM 8562/RM 8563	
		ω_{45}	ω_{46}	$\eta_{45} (10^3)$	$\eta_{46} (10^3)$	$\eta_{45} (10^3)$	$\eta_{46} (10^3)$
Lab#1	3	49	89	--	--	0.53	1.72
Lab#2	0	26	69	1.30	2.24	2.55	3.49
Lab#3	1	127	265	0.48*	0.89*	-1.08 [†]	5.26
Lab#4	1	135	68	0.25*	0.18*	1.45	2.24
Lab#5	2	111	111	0.25	2.37	0.10	-0.69 [†]
Lab#6	0	126	171	1.17	2.33	1.67	-0.67 [†]
Lab#7	9	580	678	1.48	4.53	3.85	5.16

[‡] The full analysis sequence called for 49 sample runs (see Appendix 2). Because of measurement replication, these missing samples did not prevent us from obtaining complete sets of averaged results.

[†] See text for a discussion of negative values and the comparability between the methods for determining η values.

* These values of η were determined through a follow-up exercise occurring many months after completion of the original measurements, therefore they may be less applicable to the correction for cross contamination.

Table 4A: Uncorrected $\delta^{45}\text{CO}_2$ Measurements (vs. WRG, ‰)

	Lab 1		Lab 2		Lab 3		Lab 4		Lab 5		Lab 6		Lab 7		Lab 8	
	\bar{x}	u_i														
NBS19	-0.03	0.03	12.01	0.05	21.68	0.03	5.05	0.01	14.64	0.02	11.74	0.03	39.02	0.04	-0.80	0.30
NBS18	-7.23	0.02	4.74	0.01	14.29	0.05	-2.22	0.01	7.29	0.02	4.46	0.02	31.64	0.01	-7.72	0.35
IAEA CO-9	-46.52	0.02	-34.79	0.04	-25.98	0.02	-41.52	0.09	-32.50	0.03	-35.11	0.03	-9.00	0.04	-26.12	0.05
LSVEC	-45.78	0.46	-34.47	0.08	-25.52	0.02	-41.11	0.05	-32.18	0.03	-34.82	0.06	-8.98	0.12	-31.38	0.43
LSG	-4.79	0.01	0.00	0.02	0.04	0.01	0.01	0.06	-0.01	0.02	6.50	0.02	0.13	0.01	0.02	0.08
RM 8562	-5.90	0.07	6.08	0.01	15.68	0.00	-0.87	0.01	8.70	0.05	5.90	0.01	33.09	0.02	-6.47	0.42
RM 8563	-41.71	0.01	-30.02	0.02	-21.02	0.00	-36.79	0.00	-27.67	0.01	-30.26	0.04	-3.89	0.11	-40.38	0.46
RM 8564	-11.86	0.01	0.10	0.02	9.59	0.01	-6.85	0.03	2.60	0.03	-0.19	0.02	26.89	0.00	-12.17	0.25
VSMOW	-4.41	0.10	0.36	0.04	0.38	0.02	0.70	0.01	-29.89	0.03	6.96	0.02	25.07	0.07	-8.64	0.50
SLAP	-6.28	0.04	-1.76	0.01	-1.62	0.02	-1.37	0.19	-31.85	0.01	4.96	0.01	22.65	0.03	-10.45	0.46

Table 4B: Uncorrected $\delta^{46}\text{CO}_2$ Measurements (vs. WRG, ‰)

	Lab 1		Lab 2		Lab 3		Lab 4		Lab 5		Lab 6		Lab 7		Lab 8	
	\bar{x}	u_i														
NBS19	0.62	0.06	6.71	0.05	6.89	0.03	13.13	0.06	10.54	0.05	6.13	0.05	23.22	0.25	-0.08	0.26
NBS18	-20.37	0.07	-14.35	0.02	-14.38	0.03	-8.29	0.02	-10.67	0.03	-14.91	0.06	2.76	0.10	-22.52	0.46
IAEA CO-9	-12.83	0.10	-6.66	0.04	-6.53	0.02	-0.82	0.05	-2.92	0.06	-7.36	0.08	10.16	0.11	-13.82	0.09
LSVEC	-23.79	0.37	-18.09	0.05	-17.61	0.04	-11.71	0.07	-14.52	0.04	-18.56	0.10	-1.16	0.25	-26.49	0.12
LSG	-11.24	0.02	0.02	0.02	0.01	0.02	-0.08	0.02	-0.00	0.05	-2.91	0.04	-0.11	0.02	0.00	0.11
RM 8562	-15.82	0.00	-9.68	0.06	-9.62	0.01	-3.54	0.01	-5.93	0.07	-10.14	0.00	7.32	0.00	-17.77	0.32
RM 8563	-31.08	0.01	-24.99	0.03	-24.87	0.00	-18.98	0.00	-21.42	0.01	-25.56	0.04	-8.20	0.34	-34.04	0.36
RM 8564	-7.26	0.00	-1.28	0.04	-1.01	0.00	5.15	0.03	2.56	0.00	-1.71	0.04	15.79	0.22	-8.53	0.26
VSMOW	2.55	0.09	9.06	0.11	8.77	0.05	16.17	0.10	12.39	0.06	8.07	0.03	26.01	0.09	1.79	0.32
SLAP	-53.46	0.08	-46.84	0.26	-47.57	0.03	-37.66	1.23	-44.16	0.04	-47.38	0.05	-30.21	0.24	-58.11	0.54

Table 5A: Corrected $\delta^{45}\text{CO}_2$ Measurements (vs. WRG, ‰)

	Lab 1		Lab 2		Lab 3		Lab 4		Lab 5		Lab 6		Lab 7	
	\bar{x}	u_i												
NBS19	-0.03	0.03	12.05	0.05	21.70	0.03	5.05	0.01	14.65	0.02	11.77	0.03	39.14	0.04
NBS18	-7.26	0.02	4.75	0.01	14.31	0.05	-2.22	0.01	7.29	0.02	4.47	0.02	31.74	0.01
IAEA CO-9	-46.69	0.02	-34.88	0.04	-26.00	0.02	-41.54	0.09	-32.51	0.03	-35.19	0.03	-9.02	0.04
LSVEC	-45.95	0.46	-34.56	0.08	-25.55	0.02	-41.13	0.05	-32.19	0.03	-34.90	0.06	-9.01	0.12
LSG	-4.79	0.01	0.00	0.02	0.04	0.01	0.01	0.06	-0.01	0.02	6.51	0.02	0.13	0.01
RM 8562	-5.92	0.07	6.09	0.01	15.70	0.00	-0.87	0.01	8.70	0.05	5.91	0.01	33.19	0.02
RM 8563	-41.86	0.01	-30.10	0.02	-21.04	0.00	-36.81	0.00	-27.68	0.01	-30.33	0.04	-3.90	0.11
RM 8564	-11.90	0.01	0.10	0.02	9.60	0.01	-6.85	0.03	2.60	0.03	-0.19	0.02	26.97	0.00
VSMOW	-4.43	0.10	0.36	0.04	0.38	0.02	0.70	0.01	-29.90	0.03	6.98	0.02	25.15	0.07
SLAP	-6.30	0.04	-1.76	0.01	-1.62	0.02	-1.37	0.19	-31.87	0.01	4.97	0.01	22.71	0.03

All delta values are corrected for cross contamination. VSMOW and SLAP values not corrected for gas dilution. Lack of GS-40 data from Lab#8 precluded the calculation of corrections

Table 5B: Corrected $\delta^{46}\text{CO}_2$ Measurements (vs. WRG, ‰)

	Lab 1		Lab 2		Lab 3		Lab 4		Lab 5		Lab 6		Lab 7	
	\bar{x}	u_i												
NBS19	0.62	0.06	6.73	0.05	6.90	0.03	13.14	0.06	10.59	0.05	6.16	0.05	23.43	0.25
NBS18	-20.44	0.07	-14.41	0.02	-14.40	0.03	-8.29	0.02	-10.72	0.03	-14.98	0.06	2.78	0.10
IAEA CO-9	-12.87	0.10	-6.69	0.04	-6.54	0.02	-0.82	0.05	-2.94	0.06	-7.40	0.08	10.25	0.11
LSVEC	-23.87	0.37	-18.17	0.05	-17.64	0.04	-11.72	0.07	-14.59	0.04	-18.65	0.10	-1.17	0.25
LSG	-11.27	0.02	0.02	0.02	0.01	0.02	-0.08	0.02	-0.00	0.05	-2.92	0.04	-0.11	0.02
RM 8562	-15.88	0.00	-9.73	0.06	-9.64	0.01	-3.54	0.01	-5.96	0.07	-10.19	0.00	7.38	0.00
RM 8563	-31.19	0.01	-25.10	0.03	-24.92	0.00	-18.99	0.00	-21.52	0.01	-25.68	0.04	-8.27	0.34
RM 8564	-7.29	0.00	-1.28	0.04	-1.01	0.00	5.15	0.03	2.57	0.00	-1.72	0.04	15.94	0.22
VSMOW	2.55	0.09	9.06	0.11	8.77	0.05	16.17	0.10	12.39	0.06	8.07	0.03	26.01	0.09
SLAP	-53.64	0.08	-47.05	0.26	-47.65	0.03	-37.68	1.23	-44.36	0.04	-47.59	0.05	-30.48	0.24

All delta values corrected for cross contamination. VSMOW and SLAP values not corrected for gas dilution. Lack of GS-40 data from Lab#8 precluded the calculation of corrections

Table 6A: $\delta^{45}\text{CO}_2$ Values (vs. NBS19-CO₂, ‰)

	Lab 1		Lab 2		Lab 3		Lab 4		Lab 5		Lab 6		Lab 7	
	\bar{x}	u_c												
NBS 18	-7.23	0.04	-7.20	0.06	-7.24	0.05	-7.23	0.01	-7.25	0.03	-7.21	0.03	-7.13	0.04
IAEA CO-9	-46.67	0.03	-46.37	0.07	-46.69	0.03	-46.35	0.09	-46.48	0.03	-46.41	0.04	-46.35	0.06
LSVEC	-45.92	0.46	-46.05	0.10	-46.25	0.03	-45.95	0.05	-46.17	0.04	-46.13	0.07	-46.34	0.13
RM 8562	-5.89	0.08	-5.88	0.05	-5.88	0.03	-5.89	0.01	-5.86	0.05	-5.79	0.03	-5.73	0.04
RM 8563	-41.83	0.03	-41.64	0.06	-41.84	0.03	-41.65	0.01	-41.72	0.02	-41.61	0.03	-41.42	0.12
RM 8564	-11.87	0.03	-11.80	0.06	-11.85	0.03	-11.84	0.03	-11.87	0.03	-11.82	0.04	-11.72	0.04
VSMOW	-4.40	0.10	-11.54	0.07	-20.87	0.04	-4.33	0.02	-43.91	0.04	-4.73	0.03	-13.47	0.08
SLAP	-6.27	0.05	-13.65	0.05	-22.83	0.03	-6.39	0.19	-45.85	0.02	-6.71	0.03	-15.81	0.05

All delta values corrected for cross contamination. VSMOW and SLAP values not corrected for gas dilution.

Values in shaded cells have combined standard uncertainties greater than 0.2 ‰. These values have been excluded from further calculations.

Table 6B: $\delta^{46}\text{CO}_2$ Values (vs. NBS19-CO₂, ‰)

	Lab 1		Lab 2		Lab 3		Lab 4		Lab 5		Lab 6		Lab 7	
	\bar{x}	u_c												
NBS 18	-21.05	0.09	-21.01	0.05	-21.16	0.05	-21.15	0.06	-21.09	0.06	-21.01	0.08	-20.18	0.27
IAEA CO-9	-13.48	0.11	-13.33	0.06	-13.35	0.04	-13.77	0.08	-13.38	0.08	-13.48	0.10	-12.88	0.27
LSVEC	-24.47	0.38	-24.73	0.07	-24.37	0.05	-24.53	0.09	-24.91	0.06	-24.66	0.11	-24.04	0.36
RM 8562	-16.48	0.06	-16.35	0.07	-16.43	0.04	-16.47	0.06	-16.38	0.08	-16.25	0.05	-15.68	0.25
RM 8563	-31.79	0.06	-31.62	0.06	-31.60	0.03	-31.71	0.06	-31.77	0.05	-31.65	0.06	-30.98	0.42
RM 8564	-7.90	0.06	-7.96	0.06	-7.86	0.03	-7.88	0.07	-7.93	0.05	-7.83	0.06	-7.32	0.33
VSMOW	1.93	0.11	2.31	0.12	1.86	0.06	2.99	0.11	1.78	0.08	1.90	0.06	2.52	0.27
SLAP	-54.22	0.10	-53.43	0.26	-54.17	0.05	-50.16	1.23	-54.38	0.07	-53.42	0.07	-52.68	0.35

All delta values corrected for cross contamination. VSMOW and SLAP values not corrected for gas dilution.

Values in shaded cells have combined standard uncertainties greater than 0.2 ‰. These values have been excluded from further calculations.

Table 7. Reported Values of Unrestricted Variables

Discretionary Variables	CODE	Lab#1	Lab#2	Lab#3	Lab#4	Lab#5	Lab#6	Lab#7
Phosphoric Acid								
Prep Method	I	3	2	3	3	3	1	3
History	I	1	5	2	7	4	1	2
Obs.Sp. Gravity	R	1.93	1.918	1.955	1.91	1.91	1.93	1.92
Hydrometer (ID#)	N	732101	732092	732073	732099	29481	732067	NR
Temp. (deg. C)	R	20	23.8	24.2	22	24.5	20.5	23
Rel.Sp. Gravity	C	1.91	1.90	1.94	1.89	1.90	1.91	1.90
Acid/Carb Reaction								
Amt.Carbonate (mg)	R	8	5	20.5	200	20	20	6
Amount Acid (mL)	R	1	0.5	3	5	2	4	5
Volume (mL)	R	8.5	20	40	57	70	70	50
Time (hr)	R	6	24	17	24	18	18.5	24
Temp. (deg. C)	R	25	25	25	30	25	25	25
Water-CO₂ Eq								
Pre-Eq Treatment	I	3	2	1	3	1	1	1
Amt. Water (mL)	R	4	0.96	2	3	3	1	4
Amt.CO ₂ (μmol)	R	332	58	350	440	200	450	30
Identity CO ₂	N	LGS	LGS	LGS	LGS	other	LGS	other
Volume (mL)	R	22.7	5.7	27	25	48	16.5	25
Temp. (deg. C)	R	25	25	25	18	25	25	25
Agitation	B	1	2	1	1	1	2	1
Time (hr)	R	17	48	16	5	18	25	24
Post-Eq Treatment	B	1	2	1	1	1	1	1
Inlet								
Storage Vessel	I	0	2	3	4	2	1	2
Storage Time	R	1	4	2	6	5	3	7
Measurement								
Instrument Manufacturer	B	1	1	1	1	1	2	2
Instrument Model	I	6	1	4	5	2	8	7
History	I	3	1	0	0	4	2	0
Refill	I	4	1	1	2	2	1	3
EvacTime (s)	R	80	60	30	60	120	40	120
InletPressure (mbar)	R	30	33	NR	47	42	25	NR
IdleTime (s)	R	14	16	8	10	30	15	12
IntegrationTime (s)	R	8	8	8	8	16	10	20
Elect.Energy (eV)	R	90	80	72	10	60	58	60.9
Accel.Voltage (keV)	R	3	9.88	8	3	6.6	2.77	3.5
WRG (δ ⁴⁵ v.NBS19) ‰	C	0.03	-11.90	-21.24	-5.04	-14.44	-11.63	-37.67
WRG (δ ⁴⁶ v.NBS19) ‰	C	-0.62	-6.69	-6.85	-13.02	-10.48	-6.12	-22.90

Further explanation in text and on website version at

<http://www.cstl.nist.gov/div837/837.01/outputs/NIMICONI.xls>.

Codes: I – integer variable based on interpretation of textual information provided by participants

R – reported continuous variable

N – informational variable

C – calculated continuous variable

B – binary variable

NR – not recorded

Table 8. Results of the Current Exercise, Comparison to Previous Reference Values[‡], and Recommended Values

Reference Material [Ⓛ]	Expression	Previous Reference Value [‡]	Uncertainty*	Mean Cross Contamination Correction	Mean Value from Inter-comparison [†]	Uncertainty*	Recommended Value**	Uncertainty*
NBS 19 [†] (CO ₂)	$\delta^{13}\text{C}_{\text{VPDB}}$ $\delta^{18}\text{O}_{\text{VPDB.CO2}}$	+1.95 -2.20	Exact Exact	0 0	+1.95 -2.20	Exact Exact	+1.95 -2.20	Exact Exact
NBS 18 (CO ₂)	$\delta^{13}\text{C}_{\text{VPDB}}$ $\delta^{18}\text{O}_{\text{VPDB.CO2}}$	-5.01 -22.97	0.06 (u_i) 0.11 (u_i)	-0.01 -0.07	-5.06 -23.24	0.02 (u_i) 0.07 (u_i)	-5.06 -23.01	0.03 (u_c) 0.22 (u_c)
LSVEC (CO ₂)	$\delta^{13}\text{C}_{\text{VPDB}}$ $\delta^{18}\text{O}_{\text{VPDB.CO2}}$	-46.44 -26.46	0.21 (u_i) 0.48 (u_i)	-0.05 -0.07	-46.53 -26.71	0.12 (u_i) 0.20 (u_i)	-46.53 -26.44	0.12 (u_c) 0.30 (u_c)
IAEA-CO-9 (CO ₂)	$\delta^{13}\text{C}_{\text{VPDB}}$ $\delta^{18}\text{O}_{\text{VPDB.CO2}}$	-47.13 -15.28	0.21 (u_i) 0.20 (u_i)	-0.06 -0.04	-47.31 -15.55	0.14 (u_i) 0.16 (u_i)	-47.31 -15.40	0.14 (u_c) 0.26 (u_c)
RM 8562 (CO ₂)	$\delta^{13}\text{C}_{\text{VPDB}}$ $\delta^{18}\text{O}_{\text{VPDB.CO2}}$	-3.76 -18.51	0.03 (u_c) 0.11 (u_c)	-0.01 -0.05	-3.76 -18.56	0.04 (u_i) 0.09 (u_i)	-3.76 -18.49	0.03 (u_c) 0.22 (u_c)
RM 8563 (CO ₂)	$\delta^{13}\text{C}_{\text{VPDB}}$ $\delta^{18}\text{O}_{\text{VPDB.CO2}}$	-41.56 -33.63	0.06 (u_c) 0.11 (u_c)	-0.05 -0.10	-41.57 -33.76	0.09 (u_i) 0.08 (u_i)	-41.56 -33.52	0.04 (u_c) 0.24 (u_c)
RM 8564 (CO ₂)	$\delta^{13}\text{C}_{\text{VPDB}}$ $\delta^{18}\text{O}_{\text{VPDB.CO2}}$	-10.45 -9.96	0.04 (u_c) 0.10 (u_c)	-0.02 -0.03	-10.44 -10.06	0.03 (u_i) 0.05 (u_i)	-10.45 -10.09	0.03 (u_c) 0.20 (u_c)
VSMOW [‡] (CO ₂)	$\delta^{18}\text{O}_{\text{VPDB.CO2}}$	-0.28	0.00	+0.00	-0.17	0.18 (u_i)	+0.15	0.18 (u_c)
SLAP [‡] (CO ₂)	$\delta^{18}\text{O}_{\text{VPDB.CO2}}$	-55.76	0.00	-0.19	-56.30	0.26 (u_i)	-55.36	0.26 (u_c)

[‡] All delta values and uncertainties are expressed as per mill (‰) deviations from the stated reference. Results in Stichler (1995) supersede 1992 NIST Report of Investigation for RMs 8543-8546 (Appendix 5)

[Ⓛ] RMs in form of carbon dioxide: carbonates digested with 100% H₃PO₄ at 25 degrees Celsius; waters equilibrated with CO₂ at 25 °C and corrected for dilution where the molar ratio (H₂O/CO₂) → ∞

* Uncertainty expressed as Type A standard uncertainty (u_i) or combined (u_c) standard uncertainty (ISO, 1993). Combined uncertainties may be less than u_i estimates from the intercomparison since u_c values derive from NIST measurements (see text).

[†] Oxygen isotope assumptions: VPDB-calcite ratios ($^{17}\text{R}_{\text{ref}}=0.0003788666$, $^{18}\text{R}_{\text{ref}}=0.00206716068$); isotope relationship factor (λ_i) = 0.5; ($\alpha_{\text{CO}_2\text{-calcite}}^{18}$) = 1.01025

[‡] Value assignments of NBS 19 (vs. VPDB) and SLAP (vs. VSMOW) are defined exactly; the reported precisions of VSMOW (vs. VPDB-CO₂) and SLAP (vs. VPDB-CO₂) are dictated by the precision of the conversion between scales: $\delta^{18}\text{O}_{\text{VSMOW}} = 1.03092 \delta^{18}\text{O}_{\text{VPDB}} + 30.92$ (Coplen, Kendall and Hopple 1983), where original coefficients are amended based on ($\alpha_{\text{CO}_2\text{-H}_2\text{O}}^{18}$) = 1.04120 and $\delta^{18}\text{O}_{\text{VPDB}}$ (NBS19-calcite) = -2.20 ‰.

** Oxygen isotope value assignments corrected 10/19/04 (normalized so that $\delta^{18}\text{O}_{\text{VPDB}}$ of NBS 19 = -2.2 ‰ and $\delta^{18}\text{O}_{\text{SLAP/VSMOW}} = -55.5$ ‰). Coplen (1988).

TABLE 9. Verified $\Delta\delta$ Measurements Among NIST Reference Gases

Sample vs. Reference	$\delta^{45}\text{CO}_2$ (‰), and u_i †	$\delta^{46}\text{CO}_2$ (‰), and u_i †	$\delta^{47}\text{CO}_2$ (‰), and u_i †	$\delta^{47}\text{CO}_2$ expected (‰) \pm U ‡
LRG-3 vs. LRG-2	-36.041 (0.004)	-15.451 (0.010)	-51.78 (0.06)	-51.78 \pm 0.04
LRG-4 vs. LRG-2	-5.963 (0.007)	+8.760 (0.009)	+2.38 (0.06)	+2.42 \pm 0.06
LRG-2 vs. LRG-2	-0.003 (0.006)	-0.008 (0.006)	+0.01 (0.06)	-0.01 \pm 0.04
RM8562 vs. LRG-2	-0.013 (0.011)	0.036 (0.024)		
RM8563 vs. LRG-3	-0.002 (0.006)	0.021 (0.020)	n/a	n/a
RM8564 vs. LRG-4	-0.056 (0.010)	-0.023 (0.027)		
RM8563 vs. RM8562	-36.028 (0.014)	-15.458 (0.033)		
RM8564 vs. RM8562	-6.010 (0.017)	8.689 (0.038)		

† Errors (in parentheses) are standard uncertainties about the mean.

‡ The expanded combined standard uncertainty (U) = $k \cdot u_c$, where the value of k (the coverage factor) equals 2, and u_c combines (in quadrature) the imprecision (u_i) in the $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ measurements and the uncertainty in λ for calculation of the expected $\delta^{47}\text{CO}_2$ value.

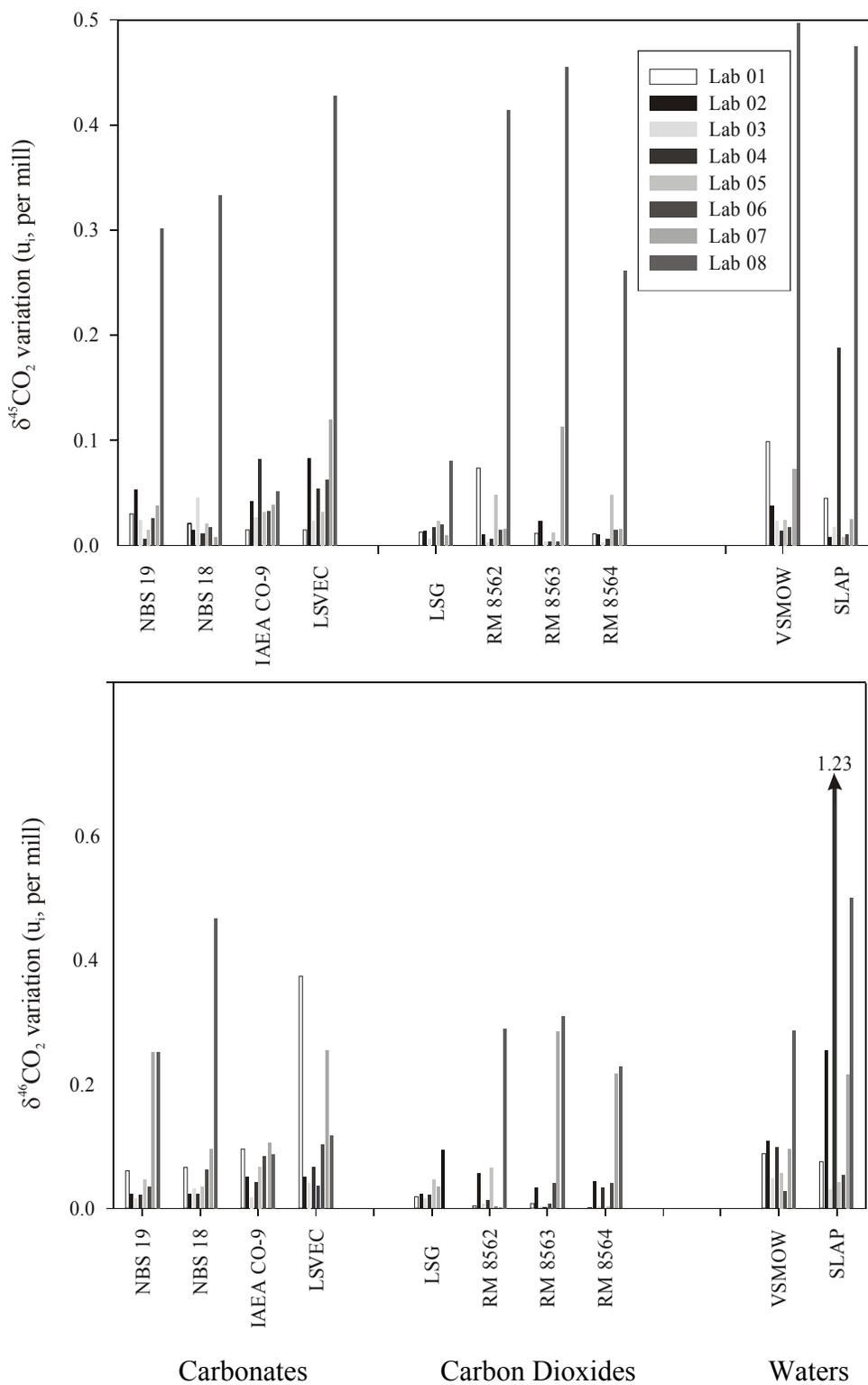


Figure 1. Measurement repeatability in participating laboratories. Lab 8 had severe instrumental difficulties, reflected by the high variability in reported data from sample replicates. In general, the carbon dioxide samples were the most repeatable, followed by the carbonate samples and the water samples.

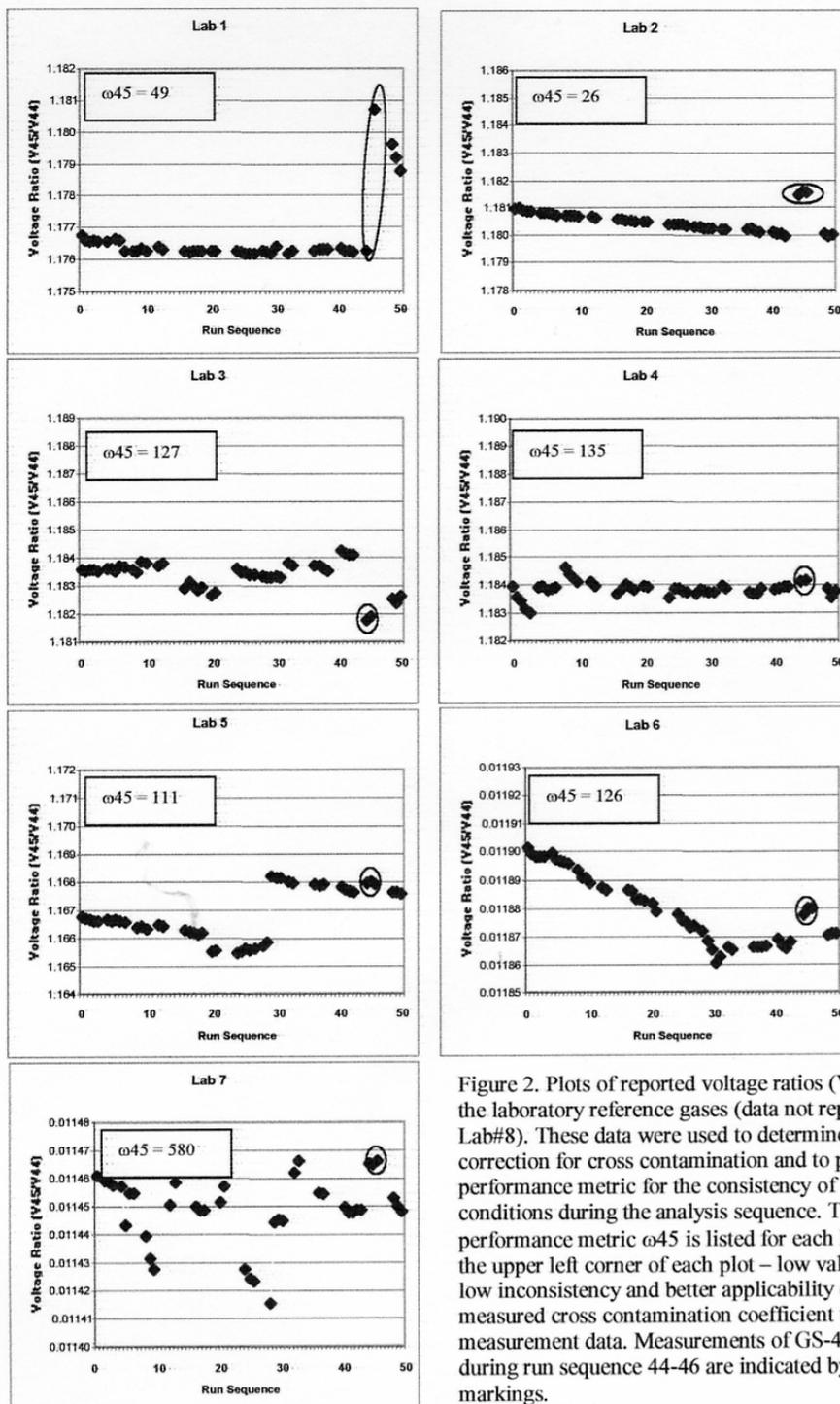


Figure 2. Plots of reported voltage ratios (V45/V44) for the laboratory reference gases (data not reported from Lab#8). These data were used to determine the correction for cross contamination and to provide a performance metric for the consistency of ion source conditions during the analysis sequence. The performance metric ω_{45} is listed for each laboratory in the upper left corner of each plot – low values signify low inconsistency and better applicability of the measured cross contamination coefficient to the measurement data. Measurements of GS-40 replicates during run sequence 44-46 are indicated by the oval markings.

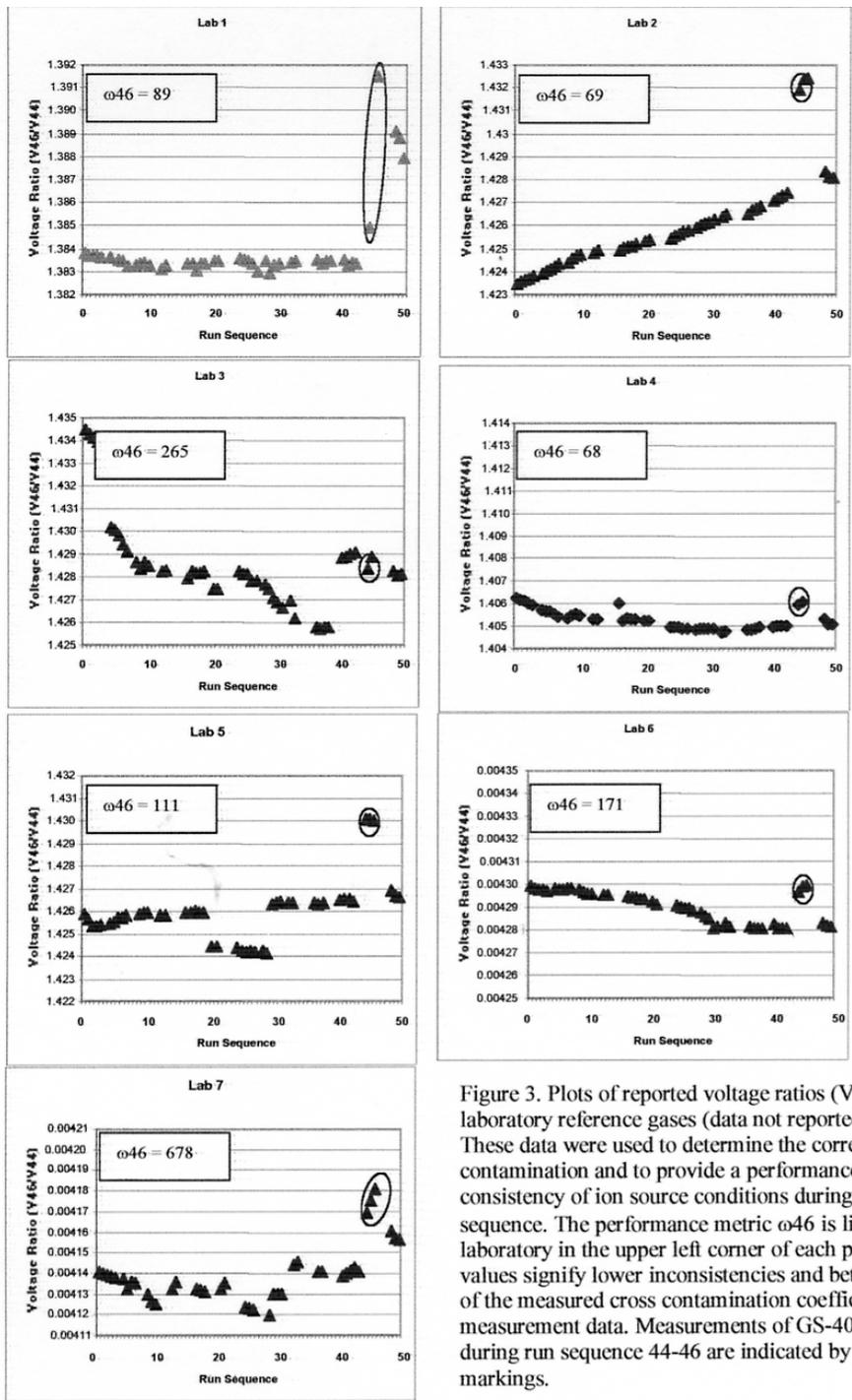


Figure 3. Plots of reported voltage ratios (V46/V44) for the laboratory reference gases (data not reported from Lab#8). These data were used to determine the correction for cross contamination and to provide a performance metric for the consistency of ion source conditions during the analysis sequence. The performance metric ω_{46} is listed for each laboratory in the upper left corner of each plot – lower values signify lower inconsistencies and better applicability of the measured cross contamination coefficient to the measurement data. Measurements of GS-40 replicates during run sequence 44-46 are indicated by the oval markings.

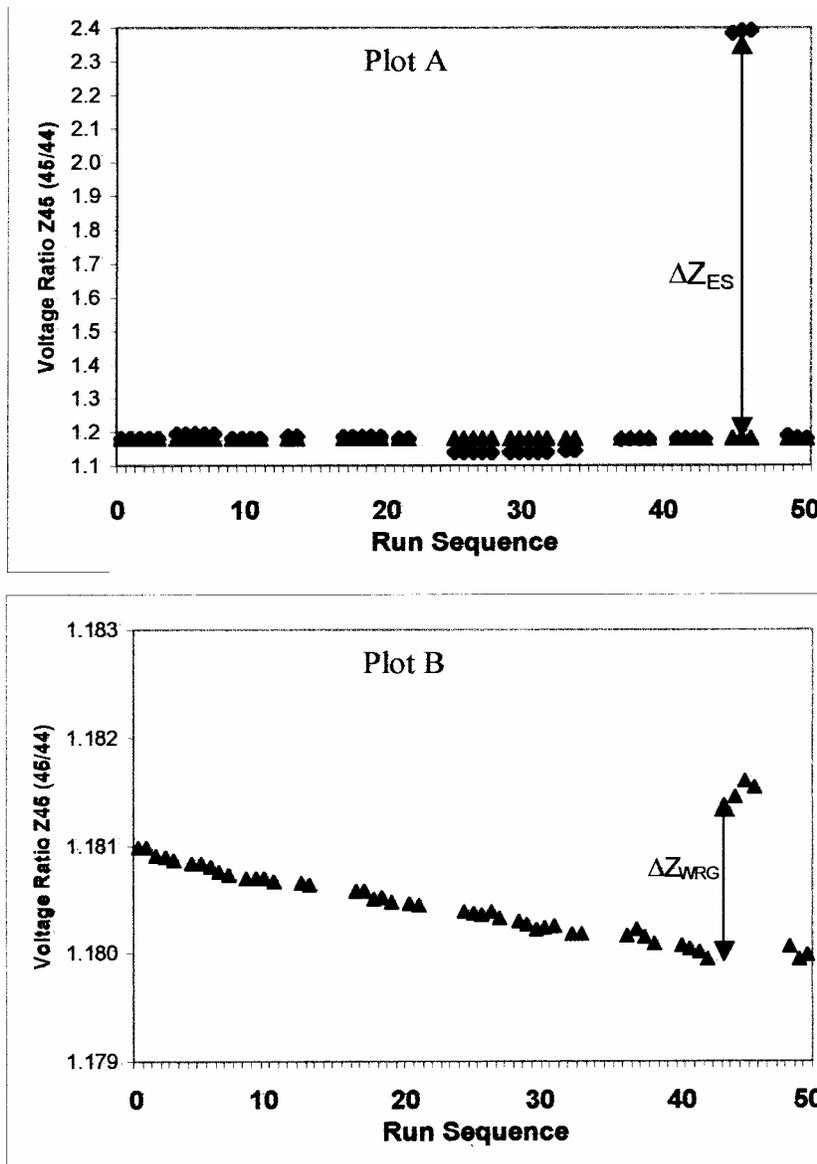


Figure 4. The determination of the cross contamination coefficient (Eq. 5) requires the measurement of the voltage ratio difference between the WRG baseline and the isotopically enhanced sample (plot A), and the voltage ratio difference between the WRG baseline and the “perturbed” WRG during the measurement of the isotopically enhanced sample (plot B). Measurements of WRG are indicated by the triangles; the diamonds indicate measurements of samples.

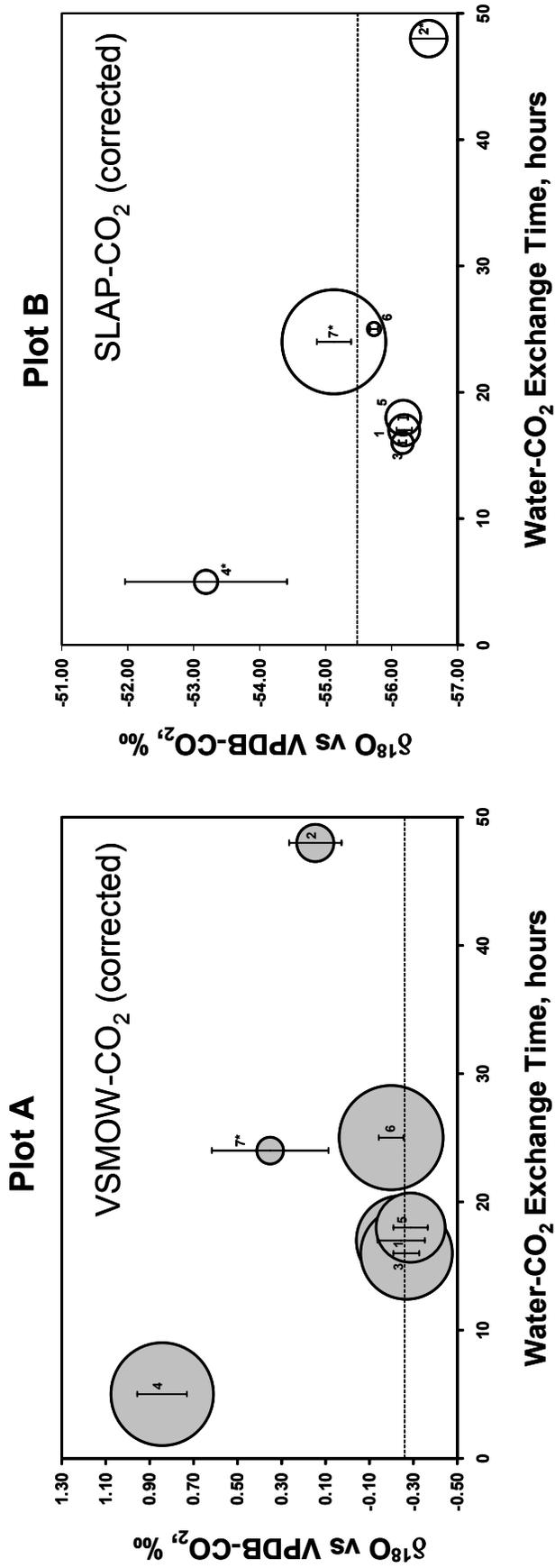


Figure 5. Bubble scatter plots of water sample variables. Plot A: $\delta^{18}\text{O}$ of VSMOW-CO₂ vs. water-CO₂ exchange time vs. amount of CO₂ used (proportional to shaded bubble size). Plot B: $\delta^{18}\text{O}$ of SLAP-CO₂ vs. water-CO₂ exchange time vs. H₂O/CO₂ molar ratio (proportional to unshaded bubble size). Measurements identified with lab numbers; dashed lines designate internationally-accepted values. The error bars indicate standard uncertainties of the $\delta^{18}\text{O}$ values from measurement replication, but do not include influences from unrestricted variables such as those specified here. Asterisks indicate data that had been excluded earlier due to performance metrics.

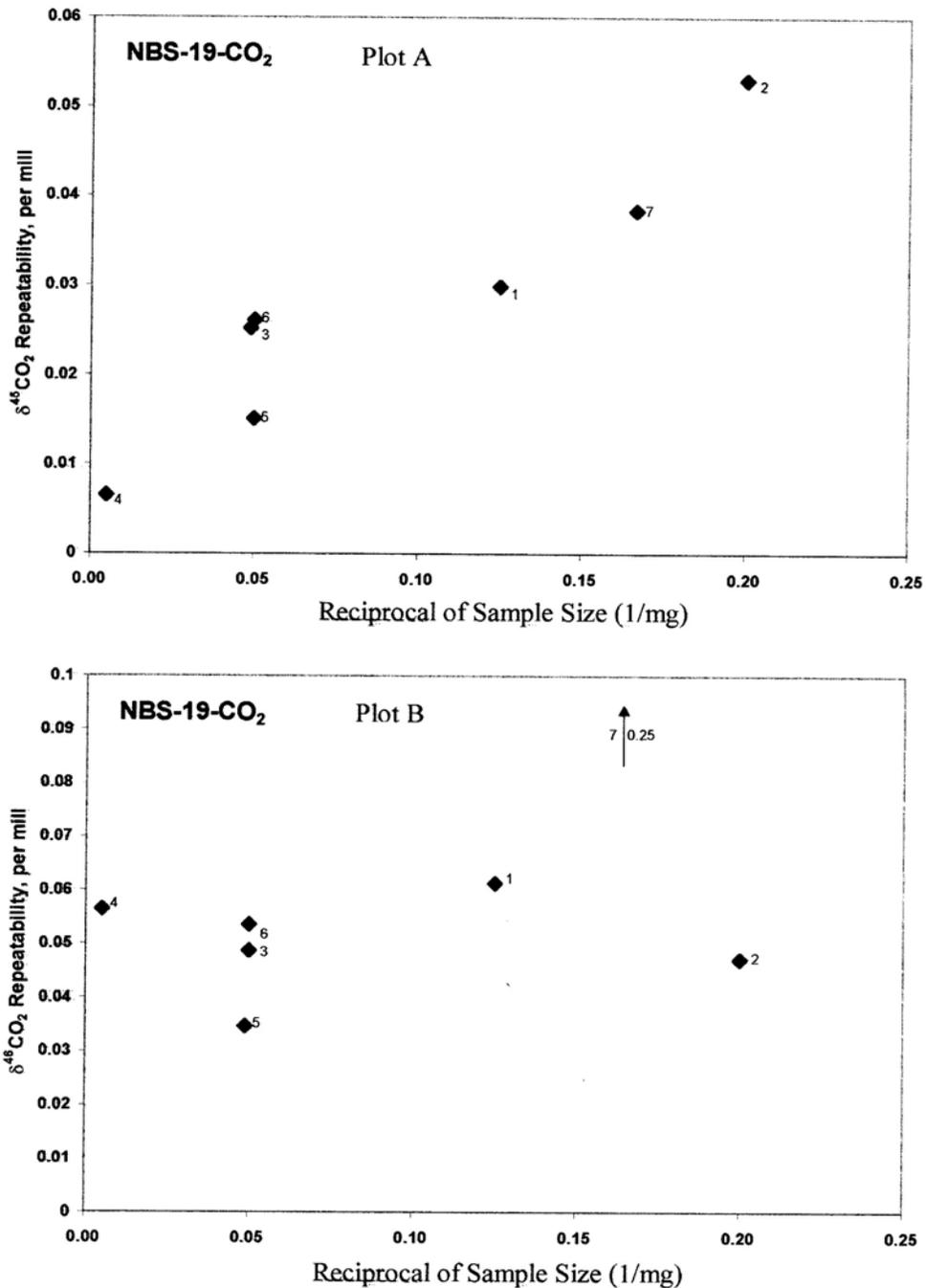


Figure 6. The effects of NBS-19 carbonate sample size (plotted as reciprocal) on the repeatability of $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ measurements against a WRG. Data in plot A indicate that uncertainty in the realization of the VPDB carbon isotope ratio scale may be minimized by using at least 20 mg of carbonate per NBS-19 sample replicate. In contrast, the amount of NBS-19 carbonate was inconsequential in the realization of the VPDB oxygen isotope ratio scale (plot B) where other factors play a more significant role in inducing variation.

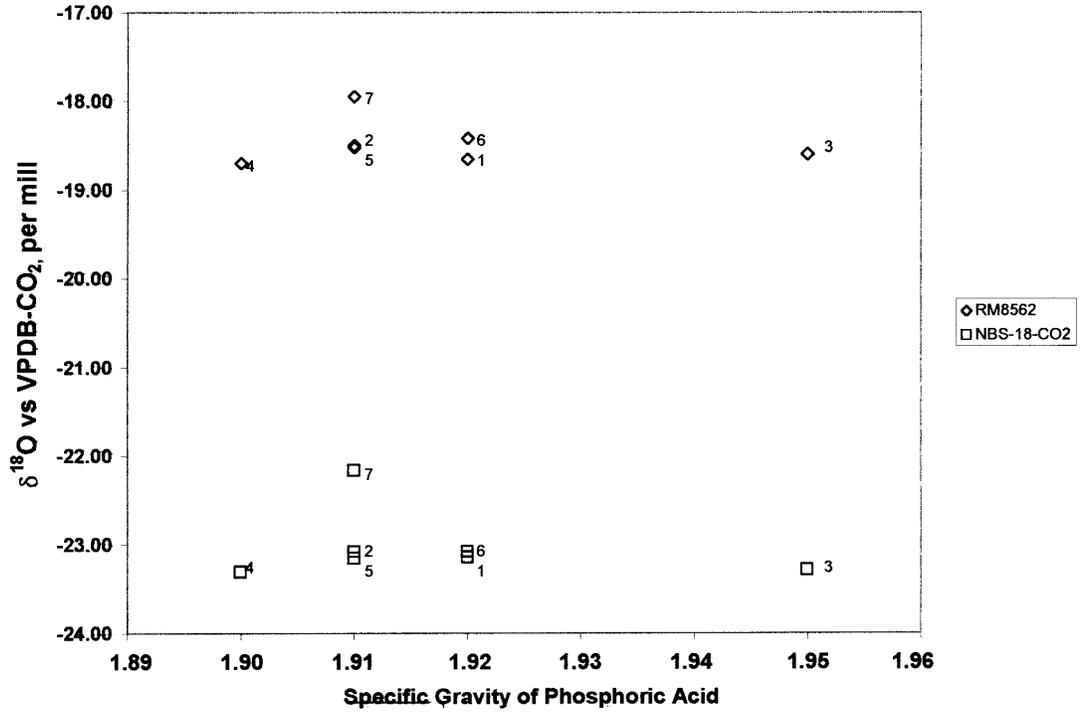


Figure 7. Scatter plots of $\delta^{18}\text{O}$ results for RM 8562 and NBS-18- CO_2 vs. the specific gravity of the phosphoric acid used for the carbonate digestions. Data identified with lab numbers. Since results are normalized to the measurements of NBS-19- CO_2 we compare a carbonate sample and non-carbonate sample to investigate whether specific gravity (hence the water content of the acid) has an effect on the $\delta^{18}\text{O}$ results. Neither type of sample shows a dependence on the specific gravity within the range of this study.

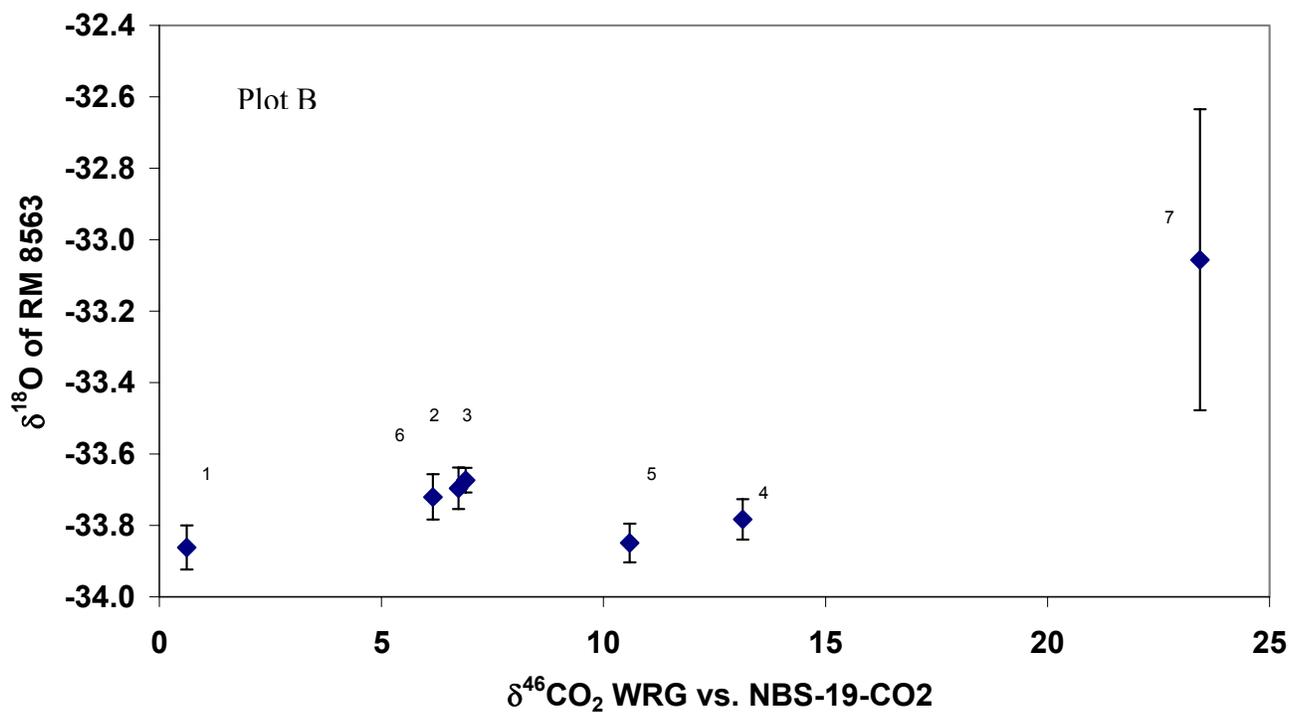
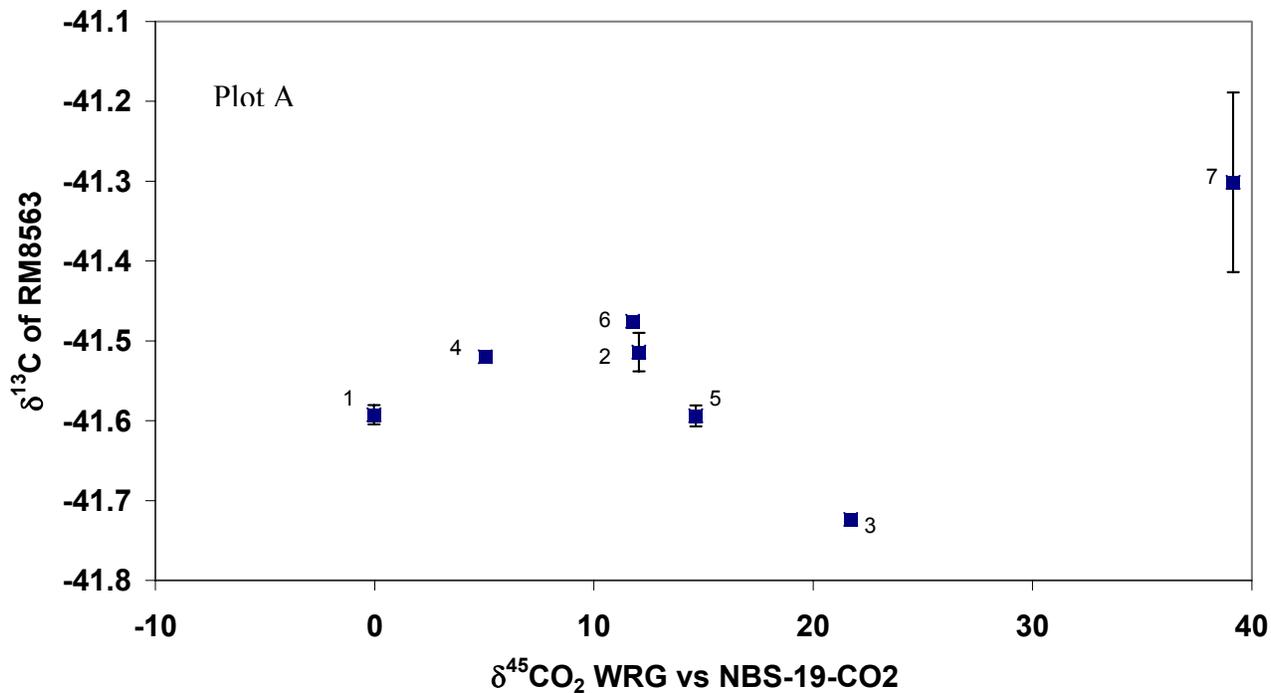


Figure 8. Plots of Working Reference Gas (WRG) compositions against the results of RM 8563. Error bars are standard uncertainties of the measurements, but do not include effects of unrestricted variables. Neither plot suggests an obvious bivariate relationship, a conclusion substantiated by multivariate Principal Components Analysis on the CO₂ samples.

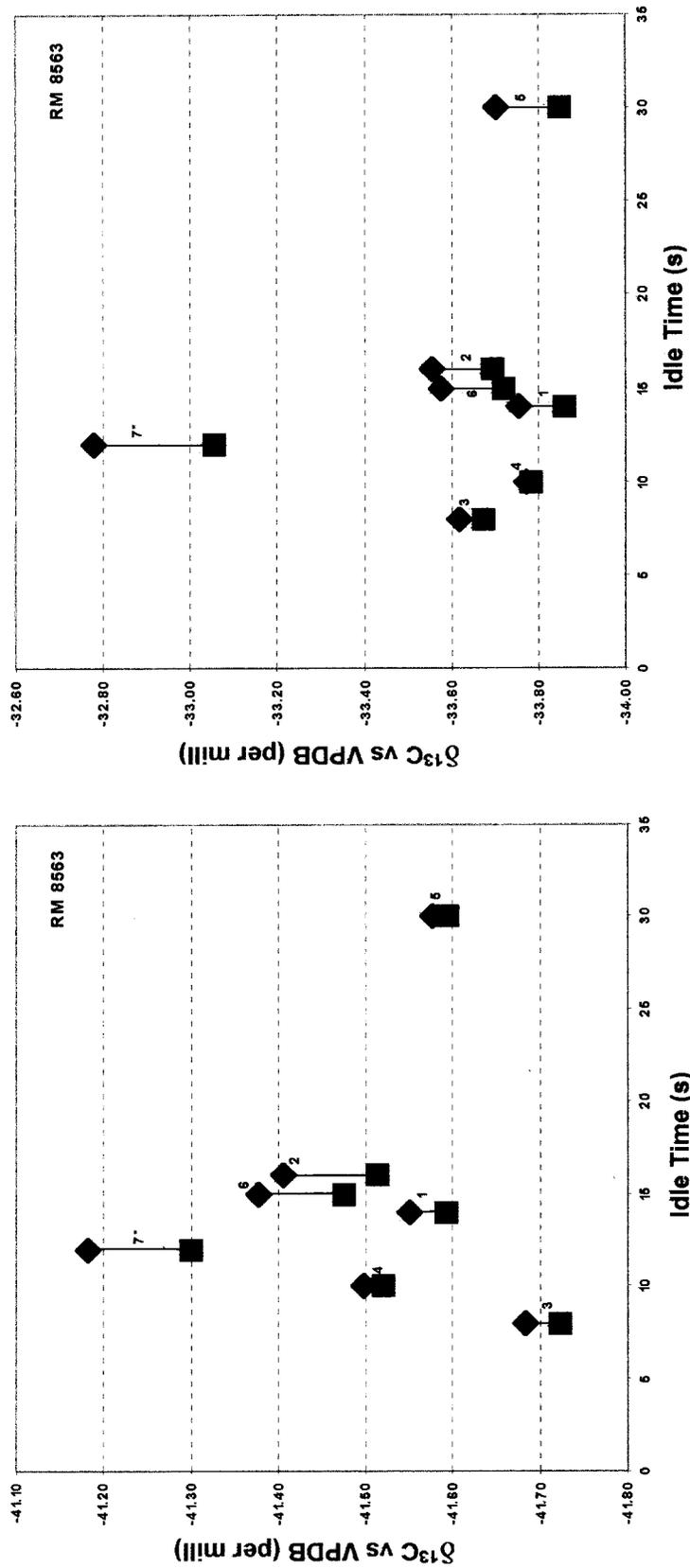


Figure 9. Sample-reference switchover time (idle time) plotted against $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ results for RM 8563, uncorrected (diamonds) and corrected (squares) for cross contamination. Points are identified by laboratory number; those with an asterisk had been excluded from the value assignment process based on performance metrics.

**APPENDIX 1:
Mandatory Procedures**

Sample Preparation

- General
 - ◆ It is mandatory that all samples be measured as soon as possible after being prepared. While less than 24 hours is preferable, the IAEA-TWG realizes that this may be impractical. The selection of appropriate interim CO₂ storage vessels is discretionary. When ready for measurement, each sample of CO₂ must be introduced into the sample inlet consistently, minimizing potential differences in isotopic fractionation among and across samples from the three different source types: carbonates, waters, and breakseals. The procedures addressing this concern are discretionary.
- Carbonates
 - ◆ Bottles of NBS-19 limestone (RM8544), NBS-18 carbonatite (RM8543), LSVEC lithium carbonate (RM8545), and IAEA-CO-9 barium carbonate (RM8566) are provided, each containing 0.5 grams of material. For each replicate, aliquants of carbonate standard must be reacted with 100% phosphoric acid at 25.0 °C to generate the CO₂ samples. Acid preparation, the amounts of acid and carbonate, reaction volume and time must be identical across the samples in your laboratory. The particular values selected for these factors are discretionary.
- Breakseals
 - ◆ Each tubular breakseal contains pure CO₂ at a pressure near 0.9 bar (NIST RM8562-8564) or 0.35 bar (CIO GS-40). Lightly score the tube and break in a clean, dry and evacuated tube cracker. Immediately, the gas should be cryogenically transferred into another port or interim storage vessel. Note the pressure of non-condensable gas.
- Water Equilibrations
 - ◆ Vials of VSMOW (RM8535) and SLAP (RM8537) standard waters are provided, each containing 20 mL. This should be sufficient for four replications each. Select a single Laboratory Standard Gas (LSG) for all equilibrations; the relative amounts of LSG and water used are discretionary. The system used for the equilibrations must allow complete isotopic exchange between the LSG and water at 25.0 °C, and deliver dry CO₂ to the sample inlet without further isotopic fractionation. The procedures for introduction of the CO₂ gas into the water vessel and the prior evacuation of this vessel are discretionary. The IAEA-TWG recommends a manual system, without capillaries, where the CO₂ may be extracted quasi-instantaneously, with experimental procedures similar to those reported in Epstein and Mayeda (1953) *Geochim. Cosmochim. Acta* **4**, 213 (but using a smaller volume system).
- Measurements
 - Acid Density
 - ◆ A hydrometer and ungraduated cylinder are provided for measuring the density of the phosphoric acid. The hydrometers used in this exercise are uniquely numbered, closely matched, and calibrated relative to each other. The acid must be thermally equilibrated with the hydrometer and cylinder (i.e., kept together in the same room overnight) before taking the measurement and the temperature recorded to the nearest degree Celsius.
 - ◆ Measurement Procedure:
 1. Rinse the hydrometer and cylinder with methanol three times and dry with a lint-free cloth.
 2. Allow the hydrometer, ungraduated cylinder, and the phosphoric acid to equilibrate thermally overnight to a stable temperature between 20 °C to 25 °C.
 3. Place approximately 50 ml of the equilibrated phosphoric acid into the cylinder, without introducing bubbles.

4. Carefully place the hydrometer into the liquid. The position of the hydrometer should be adjusted to avoid contact with the side or bottom of the cylinder. If the hydrometer is resting on the bottom of the cylinder, more phosphoric acid must be added. Take the density reading after the hydrometer level has reached a steady state (about 3 minutes) by reading at the bottom of the meniscus.
- Carbon Dioxide
 - ◆ Isotope measurements must be performed by the classical dual inlet technique, **and all must be performed in a single day** (see general note on Sample Preparation above) .
 - ◆ A single working reference gas (WRG) must be used on the “standard/reference” side of the inlet for **all** measurements; refill procedures used for the WRG during the exercise are discretionary.
 - ◆ A single laboratory standard gas (LSG) must be identified, for measurements on the “sample” side of the inlet, **and** as the CO₂ used for the water equilibrations. If possible, the LSG should be similar in isotopic composition to the WRG – preferably from the same source.
 - ◆ All measurements must utilize a single, matched inlet pressure for the sample and WRG.
 - ◆ All measurements must be replicated (reproduced) using independent aliquots of the samples; if time permits, measurement replication on any sample is allowed.
 - ◆ All measurements must utilize identical instrument settings; in particular, the major ion currents for sample and WRG, the idle time after sample-WRG changeover, the integration time, and the pumping time between the different samples. The particular instrument settings selected are discretionary, as is the inlet refill procedure for the WRG.
 - Order of measurements (see Summary Measurement Reporting Form)
 1. LSG (5 independent replications)
 2. NBS-19 CO₂ (5 independent replications)
 3. VSMOW-CO₂ (4 independent replications)
 4. RM 8562 (2 independent replications)
 5. NBS-18 CO₂ (5 independent replications)
 6. RM 8564 (2 independent replications)
 7. IAEA-CO-9 CO₂ (5 independent replications)
 8. LSVEC CO₂ (5 independent replications)
 9. RM 8563 (2 independent replications)
 10. SLAP CO₂ (4 independent replications)
 11. LSG (4 independent replications)
 12. GS-40 (3 independent replications)
 13. LSG (3 independent replications)
 - Note: GS-40
 - ◆ This gas is isotopically enhanced (2% ¹³C and 0.8% ¹⁸O), therefore the signals from the faraday cups for the minor ion beams (m/z = 45 and 46) might be saturated. It is important that any automated procedures that access the sample inlet for pressure balancing or beam centering be performed using the m/z = 44 beam. Additionally, the automated routines of some instruments may attempt to “correct” saturated signals by decreasing the pressure in the inlet at the beginning of a run. Therefore, manual control over the GS-40 measurements may be necessary to prevent this problem.

- **Data**

- Mean data must be reported as δ^{45} and δ^{46} ($\pm s$) with respect to the WRG for each independent analysis; values must be reported to the nearest 0.001 ‰ (on Summary Measurement Reporting Form)
- Background-corrected mean voltage ratios ($^{45}\text{V}/^{44}\text{V}$ and $^{46}\text{V}/^{44}\text{V}$) measured for the WRG, LSG, and GS-40 must be reported; values must be reported with eight significant digits and standard deviations must be reported to the same level of number precision (e.g.: 1.2345678 ± 0.0000057 or $0.43210567 \pm 0.00000169$)
- Except for background subtraction and (possibly) peak overlap compensation, no other corrections to the measurements should be applied

Outlier rejection is permitted, but only with discretionary caution

**APPENDIX 2:
Summary Measurement Reporting Form**

Reporting Laboratory:
Date Completed:

Sample	Order	Repl. ID	$\delta^{45} \text{ VS WRG } (\text{‰})$	$\delta^{46} \text{ VS WRG } (\text{‰})$	V_{45}/V_{44} of Sample	V_{46}/V_{44} of Sample	V_{45}/V_{44} of WRG	V_{46}/V_{44} of WRG
LSG	1	1						
	2	2						
	3	3						
	4	4						
	5	5						
NBS-19 CO ₂	6	1						
	7	2						
	8	3						
	9	4						
	10	5						
VSMOW CO ₂	11	1						
	12	2						
	13	3						
	14	4						
RM 8562	15	*						
	16	*						
NBS-18 CO ₂	17	1						
	18	2						
	19	3						
	20	4						
	21	5						
RM 8564	22	*						
	23	*						

Sample	Order	Repl. ID	$\delta^{45} \text{ VS WRG } (\text{‰})$	$\delta^{46} \text{ VS WRG } (\text{‰})$	V_{45}/N_{44} of Sample	V_{46}/N_{44} of Sample	V_{45}/N_{44} of WRG	V_{46}/N_{44} of WRG
IAEA-CO-9 CO ₂	24	1						
	25	2						
	26	3						
	27	4						
	28	5						
LSVEC CO ₂	29	1						
	30	2						
	31	3						
	32	4						
	33	5						
RM 8563	34	*						
	35	*						
SLAP CO ₂	36	1						
	37	2						
	38	3						
	39	4						
LSG	40	6						
	41	7						
	42	8						
	43	9						
	44	1						
GS-40	45	2						
	46	3						
	47	10						
LSG	48	11						
	49	12						

Please report means and standard deviations ("internal precision") for each independent analysis, with number precision as outlined in the mandatory procedures. Please indicate those values modified by outlier rejection, and the rejection criteria.
*For RMs 8562, 8563 and 8564, please report 6-digit identifiers (00xxxx or 100xxx).

APPENDIX 3:
Questionnaire regarding unrestricted variables and discretionary procedures

IAEA-NIST Coordinated Measurement Exercise for Certification of Isotopic Reference Materials: Carbon and Oxygen (1)

Participating Organization:
Primary Contact:
Analyst(s):

Discretionary Factors

- Phosphoric Acid
- Describe preparation method
- Source/manufacturer of reagents
- Preparation date
- Storage and use history
- Density reading, temperature during measurement, and hydrometer ID number (use hydrometer system supplied)
- **Acid/Carbonate Reaction** (if applicable, please note unavoidable differences for each sample)
 - Amount of carbonate used per sample (nearest 0.1 mg)
 - Amount of acid used per sample (nearest 0.1 mL)
 - Approximate volume of vessel used for acid/carbonate reaction
 - Time allowed for reaction (in hours)

- Actual temperature of system (nearest 0.1 °C)
- Post-reaction treatments, if any (e.g., agitation or warming of acid; sample drying procedures)
- **Water-CO₂ Isotopic Equilibration**
 - Pre-equilibration treatments (e.g., outgassing or modifying pH of the water sample)
 - Amount of water used per sample (nearest 0.1 mL)
 - Amount of CO₂ used per sample (in μmoles)
 - Volume of vessels used (in mL)
 - Actual temperature of system during exchange (nearest 0.1 °C)
 - Was the water agitated during exchange?
 - Time allowed for isotopic exchange (in minutes)
 - Post-equilibration treatments (e.g., drying procedures)
- **Inlet** (if applicable, please note unavoidable differences for each sample)
 - Description of interim storage vessels for CO₂ samples from carbonate and water RIMs (breakseals or valved vessels with greased stopcocks, o-rings, etc)
 - Duration of interim storage (in hours)

- Description, and notable differences, of expansion, cryogenic, and other port-to-inlet transfer procedures used for the various samples
- **Measurement**
 - Instrument model, with description of notable modifications
 - Summary of IRMS history for past year, especially regarding vacuum, venting, bakeout, and prior sample types that may influence these measurements
 - Refill protocol for working reference gas (WRG) in dual-inlet
 - Evacuation time between samples
 - Inlet pressure during measurement (in mbar)
 - Idle time between acquisitions of sample gas and WRG (in seconds)
 - Integration time of each acquisition (in seconds)
 - Electron energy used for ionization (in eV)
 - Accelerating voltage applied (in keV)
 - Outlier rejection procedures, if applicable

Other variables that may be significant (i.e. $m/z=44$ to $m/z=18$ ratio, especially for water-derived samples)

APPENDIX 4:
Individual Laboratory Results Calculated Through Four Sets of Assumptions

Assumption Set A
(IAEA recommendation - historical)
 $\lambda=0.5$
K=0.0083330

Assumption Set B
 $\lambda=0.516$
K=0.0093703

Assumption Set C
(Santrock recommendation)
 $\lambda=0.516$
K=0.0099235

Assumption Set D
(Assonov recommendation)
 $\lambda=0.528$
K=0.0102819

TABLE 10-A. Laboratory Results
Assumption Set A

lambda=0.5
S17=0.000378866601
S18=0.002067160680
K=0.0083329582

	Lab#1	Lab#2	Lab#3	Lab#4	Lab#5	Lab#6	Lab#7	Average (std dev)
$\delta^{13}\text{C}(\text{RM8562})$	-3.77	-3.78	-3.78	-3.79	-3.76	-3.69	-3.65	-3.76(0.04)
$\delta^{13}\text{C}(\text{RM8563})$	-41.59	-41.51	-41.72	-41.52	-41.59	-41.48	-41.30	-41.57(0.09)
$\delta^{13}\text{C}(\text{RM8564})$	-10.45	-10.41	-10.45	-10.45	-10.48	-10.43	-10.33	-10.44(0.03)
$\delta^{13}\text{C}(\text{NBS18})$	-5.04	-5.04	-5.08	-5.07	-5.09	-5.04	-4.99	-5.06(0.02)
$\delta^{13}\text{C}(\text{IAEA-CO9})$	-47.38	-47.20	-47.54	-47.17	-47.32	-47.24	-47.19	-47.31(0.14)
$\delta^{13}\text{C}(\text{LSVEC})$	-46.21	-46.46	-46.69	-46.36	-46.59	-46.55	-46.80	-46.53(0.12)
$\delta^{13}\text{C}(\text{VSMOW})$	-2.81	-10.48	-20.44	-2.78	-45.08	-3.18	-12.54	n/a
$\delta^{13}\text{C}(\text{SLAP})$	-2.88	-10.81	-20.61	-3.16	-45.22	-3.40	-13.15	n/a
$\delta^{13}\text{C}(\text{LSG})$	-2.74	-10.51	-20.49	-2.91	-13.13	-3.25	-37.31	n/a
$\delta^{18}\text{O}(\text{RM8562})$	-18.65	-18.52	-18.59	-18.63	-18.54	-18.42	-17.85	-18.56(0.09)
$\delta^{18}\text{O}(\text{RM8563})$	-33.86	-33.70	-33.67	-33.78	-33.85	-33.72	-33.06	-33.76(0.08)
$\delta^{18}\text{O}(\text{RM8564})$	-10.07	-10.13	-10.02	-10.05	-10.10	-10.00	-9.49	-10.06(0.05)
$\delta^{18}\text{O}(\text{NBS18})$	-23.21	-23.17	-23.32	-23.31	-23.25	-23.17	-22.34	-23.24(0.07)
$\delta^{18}\text{O}(\text{IAEA-CO9})$	-15.56	-15.42	-15.43	-15.86	-15.47	-15.56	-14.96	-15.55(0.16)
$\delta^{18}\text{O}(\text{LSVEC})$	-26.54	-26.81	-26.44	-26.60	-26.98	-26.73	-26.12	-26.71(0.20)
$\delta^{18}\text{O}(\text{VSMOW})$	-0.24	0.15	-0.27	0.84	-0.29	-0.20	0.35	-0.17(0.18)
$\delta^{18}\text{O}(\text{SLAP})$	-56.42	-55.59	-56.42	-52.39	-56.45	-55.92	-54.79	-56.30(0.26)
$\delta^{18}\text{O}(\text{LSG})$	-14.06	-8.83	-8.99	-15.22	-12.63	-11.20	-25.10	n/a

Delta values are expressed as per mill relative differences of CO₂ derived from sample (listed) against VPDB.CO₂
Values in shaded cells are calculated from measurements outside range of performance requirements and excluded from average

Values of d13VSMOW, d13SLAP, and d13LSG are expected to be different across the laboratories, but identical within any laboratory, since these samples are derived from the same laboratory CO₂ (for Lab#5 and Lab#7, where different gases were used for LSG and water equilibration, only d13VSMOW and d13SLAP are expected to be equal).

Fit Coeff 1	0.07	0.34	0.17	0.38	0.14	0.22	0.61	0.60
Fit Coeff 2	0.07	0.18	0.09	0.19	0.10	0.11	0.43	0.09

Fit Coeff 1 is the difference between d13(VSMOW) and d13(SLAP). The sum of these for the four laboratories meeting performance criteria for these data is listed at right.

Fit Coeff 2 is the standard deviation between d13(VSMOW), d13(SLAP), and d13(LSG), except for Lab#5 and Lab#7, where d13(LSG) is excluded. The average standard deviation across the four laboratories meeting performance criteria for these data is listed at right.

TABLE 10-B. Laboratory Results

Assumption Set B

lambda=0.516
 S17=0.0003799
 S18=0.0020052
 K=0.0093703524

	Lab#1	Lab#2	Lab#3	Lab#4	Lab#5	Lab#6	Lab#7	Average (std dev)
$\delta^{13}\text{C}(\text{RM8562})$	-3.75	-3.76	-3.76	-3.76	-3.74	-3.67	-3.63	-3.74(0.04)
$\delta^{13}\text{C}(\text{RM8563})$	-41.59	-41.51	-41.72	-41.52	-41.59	-41.47	-41.30	-41.57(0.09)
$\delta^{13}\text{C}(\text{RM8564})$	-10.45	-10.41	-10.46	-10.45	-10.48	-10.43	-10.34	-10.45(0.03)
$\delta^{13}\text{C}(\text{NBS18})$	-5.02	-5.01	-5.05	-5.04	-5.06	-5.02	-4.96	-5.03(0.02)
$\delta^{13}\text{C}(\text{IAEA-CO9})$	-47.41	-47.23	-47.58	-47.20	-47.35	-47.28	-47.23	-47.34(0.14)
$\delta^{13}\text{C}(\text{LSVEC})$	-46.22	-46.48	-46.71	-46.38	-46.60	-46.57	-46.82	-46.55(0.12)
$\delta^{13}\text{C}(\text{VSMOW})$	-2.82	-10.50	-20.47	-2.80	-45.14	-3.19	-12.56	n/a
$\delta^{13}\text{C}(\text{SLAP})$	-2.79	-10.74	-20.54	-3.08	-45.19	-3.31	-13.08	n/a
$\delta^{13}\text{C}(\text{LSG})$	-2.73	-10.52	-20.51	-2.90	-13.13	-3.24	-37.32	n/a
$\delta^{18}\text{O}(\text{RM8562})$	-18.65	-18.52	-18.59	-18.63	-18.54	-18.41	-17.85	-18.56(0.09)
$\delta^{18}\text{O}(\text{RM8563})$	-33.86	-33.69	-33.67	-33.78	-33.85	-33.72	-33.05	-33.76(0.08)
$\delta^{18}\text{O}(\text{RM8564})$	-10.07	-10.13	-10.02	-10.05	-10.10	-9.99	-9.49	-10.06(0.05)
$\delta^{18}\text{O}(\text{NBS18})$	-23.21	-23.17	-23.32	-23.31	-23.25	-23.17	-22.34	-23.24(0.07)
$\delta^{18}\text{O}(\text{IAEA-CO9})$	-15.56	-15.41	-15.43	-15.86	-15.47	-15.56	-14.96	-15.55(0.16)
$\delta^{18}\text{O}(\text{LSVEC})$	-26.54	-26.80	-26.44	-26.60	-26.98	-26.73	-26.11	-26.71(0.20)
$\delta^{18}\text{O}(\text{VSMOW})$	-0.24	0.15	-0.27	0.84	-0.29	-0.20	0.35	-0.17(0.18)
$\delta^{18}\text{O}(\text{SLAP})$	-56.42	-55.59	-56.42	-52.39	-56.45	-55.92	-54.79	-56.30(0.25)
$\delta^{18}\text{O}(\text{LSG})$	-14.06	-8.83	-8.99	-15.22	-12.63	-11.20	-25.10	n/a

Delta values are expressed as per mill relative differences of CO2 derived from sample (listed) against VPDB.CO2
 Values in shaded cells are calculated from measurements outside range of performance requirements and excluded from average

Values of d13VSMOW, d13SLAP, and d13LSG are expected to be different across the laboratories, but identical within any laboratory, since these samples are derived from the same laboratory CO2 (for Lab#5 and Lab#7, where different gases were used for LSG and water equilibration, only d13VSMOW and d13SLAP are expected to be equal).

Fit Coeff 1	-0.03	0.24	0.07	0.29	0.05	0.12	0.52	0.22
Fit Coeff 2	0.05	0.13	0.04	0.15	0.03	0.06	0.37	0.04

Fit Coeff 1 is the difference between d13(VSMOW) and d13(SLAP). The sum of these for the four laboratories meeting performance criteria for these data is listed at right.

Fit Coeff 2 is the standard deviation between d13(VSMOW), d13(SLAP), and d13(LSG), except for Lab#5 and Lab#7, where d13(LSG) is excluded. The average standard deviation across the four laboratories meeting performance criteria for these data is listed at right.

TABLE 10-C. Laboratory Results

Assumption Set C

lambda=0.516
 S17=0.000402326
 S18=0.0020052
 K=0.0099234991

	Lab#1	Lab#2	Lab#3	Lab#4	Lab#5	Lab#6	Lab#7	Average (std dev)
$\delta^{13}\text{C}(\text{RM8562})$	-3.74	-3.75	-3.75	-3.75	-3.73	-3.66	-3.62	-3.73(0.04)
$\delta^{13}\text{C}(\text{RM8563})$	-41.69	-41.61	-41.83	-41.62	-41.69	-41.58	-41.40	-41.67(0.09)
$\delta^{13}\text{C}(\text{RM8564})$	-10.48	-10.44	-10.49	-10.48	-10.52	-10.46	-10.37	-10.48(0.03)
$\delta^{13}\text{C}(\text{NBS18})$	-5.00	-5.00	-5.03	-5.03	-5.05	-5.00	-4.95	-5.02(0.02)
$\delta^{13}\text{C}(\text{IAEA-CO9})$	-47.57	-47.39	-47.74	-47.36	-47.51	-47.44	-47.39	-47.50(0.14)
$\delta^{13}\text{C}(\text{LSVEC})$	-46.36	-46.61	-46.85	-46.52	-46.74	-46.70	-46.95	-46.68(0.12)
$\delta^{13}\text{C}(\text{VSMOW})$	-2.84	-10.55	-20.56	-2.82	-45.32	-3.21	-12.62	n/a
$\delta^{13}\text{C}(\text{SLAP})$	-2.70	-10.68	-20.52	-3.00	-45.26	-3.23	-13.03	n/a
$\delta^{13}\text{C}(\text{LSG})$	-2.72	-10.55	-20.58	-2.89	-13.17	-3.24	-37.42	n/a
$\delta^{18}\text{O}(\text{RM8562})$	-18.65	-18.52	-18.59	-18.63	-18.54	-18.42	-17.85	-18.56(0.09)
$\delta^{18}\text{O}(\text{RM8563})$	-33.86	-33.69	-33.67	-33.78	-33.84	-33.71	-33.05	-33.76(0.08)
$\delta^{18}\text{O}(\text{RM8564})$	-10.07	-10.13	-10.02	-10.05	-10.10	-9.99	-9.49	-10.06(0.05)
$\delta^{18}\text{O}(\text{NBS18})$	-23.21	-23.17	-23.32	-23.31	-23.25	-23.17	-22.34	-23.24(0.07)
$\delta^{18}\text{O}(\text{IAEA-CO9})$	-15.55	-15.41	-15.42	-15.85	-15.46	-15.55	-14.96	-15.54(0.16)
$\delta^{18}\text{O}(\text{LSVEC})$	-26.54	-26.80	-26.44	-26.60	-26.98	-26.72	-26.11	-26.71(0.20)
$\delta^{18}\text{O}(\text{VSMOW})$	-0.24	0.15	-0.26	0.84	-0.28	-0.20	0.35	-0.17(0.18)
$\delta^{18}\text{O}(\text{SLAP})$	-56.43	-55.59	-56.42	-52.39	-56.44	-55.92	-54.79	-56.30(0.25)
$\delta^{18}\text{O}(\text{LSG})$	-14.06	-8.83	-8.98	-15.22	-12.63	-11.20	-25.09	n/a

Delta values are expressed as per mill relative differences of CO2 derived from sample (listed) against VPDB.CO2
 Values in shaded cells are calculated from measurements outside range of performance requirements and excluded from average

Values of d13VSMOW, d13SLAP, and d13LSG are expected to be different across the laboratories, but identical within any laboratory, since these samples are derived from the same laboratory CO2 (for Lab#5 and Lab#7, where different gases were used for LSG and water equilibration, only d13VSMOW and d13SLAP are expected to be equal).

Fit Coeff 1	-0.14	0.13	-0.04	0.18	-0.07	0.01	0.41	-0.23
Fit Coeff 2	0.07	0.07	0.03	0.09	0.05	0.01	0.29	0.04

Fit Coeff 1 is the difference between d13(VSMOW) and d13(SLAP). The sum of these for the four laboratories meeting performance criteria for these data is listed at right.

Fit Coeff 2 is the standard deviation between d13(VSMOW), d13(SLAP), and d13(LSG), except for Lab#5 and Lab#7, where d13(LSG) is excluded. The average standard deviation across the four laboratories meeting performance criteria for these data is listed at right.

TABLE 10-D. Laboratory Results

Assumption Set D

lambda=0.528
 S17=0.000386913
 S18=0.0020052
 K=0.0102819162

	Lab#1	Lab#2	Lab#3	Lab#4	Lab#5	Lab#6	Lab#7	Average (std dev)
$\delta^{13}\text{C}(\text{RM8562})$	-3.73	-3.75	-3.74	-3.75	-3.73	-3.65	-3.61	-3.72(0.04)
$\delta^{13}\text{C}(\text{RM8563})$	-41.60	-41.52	-41.73	-41.52	-41.60	-41.48	-41.31	-41.57(0.09)
$\delta^{13}\text{C}(\text{RM8564})$	-10.45	-10.41	-10.46	-10.45	-10.49	-10.43	-10.34	-10.45(0.03)
$\delta^{13}\text{C}(\text{NBS18})$	-4.99	-4.99	-5.03	-5.02	-5.04	-4.99	-4.94	-5.01(0.02)
$\delta^{13}\text{C}(\text{IAEA-CO9})$	-47.45	-47.27	-47.62	-47.24	-47.39	-47.32	-47.27	-47.38(0.14)
$\delta^{13}\text{C}(\text{LSVEC})$	-46.25	-46.50	-46.73	-46.40	-46.63	-46.59	-46.84	-46.57(0.12)
$\delta^{13}\text{C}(\text{VSMOW})$	-2.82	-10.51	-20.50	-2.81	-45.20	-3.20	-12.58	n/a
$\delta^{13}\text{C}(\text{SLAP})$	-2.71	-10.67	-20.49	-3.02	-45.16	-3.24	-13.02	n/a
$\delta^{13}\text{C}(\text{LSG})$	-2.72	-10.52	-20.52	-2.88	-13.13	-3.23	-37.33	n/a
$\delta^{18}\text{O}(\text{RM8562})$	-18.65	-18.52	-18.59	-18.63	-18.54	-18.41	-17.85	-18.56(0.09)
$\delta^{18}\text{O}(\text{RM8563})$	-33.86	-33.69	-33.67	-33.78	-33.85	-33.72	-33.05	-33.76(0.08)
$\delta^{18}\text{O}(\text{RM8564})$	-10.07	-10.13	-10.02	-10.05	-10.10	-9.99	-9.49	-10.06(0.05)
$\delta^{18}\text{O}(\text{NBS18})$	-23.21	-23.17	-23.32	-23.31	-23.25	-23.17	-22.34	-23.24(0.07)
$\delta^{18}\text{O}(\text{IAEA-CO9})$	-15.56	-15.41	-15.43	-15.85	-15.46	-15.56	-14.96	-15.54(0.16)
$\delta^{18}\text{O}(\text{LSVEC})$	-26.54	-26.80	-26.44	-26.60	-26.98	-26.72	-26.11	-26.71(0.20)
$\delta^{18}\text{O}(\text{VSMOW})$	-0.24	0.15	-0.27	0.84	-0.28	-0.20	0.35	-0.17(0.18)
$\delta^{18}\text{O}(\text{SLAP})$	-56.42	-55.59	-56.42	-52.39	-56.44	-55.92	-54.79	-56.30(0.25)
$\delta^{18}\text{O}(\text{LSG})$	-14.06	-8.83	-8.99	-15.22	-12.63	-11.20	-25.10	n/a

Delta values are expressed as per mill relative differences of CO2 derived from sample (listed) against VPDB.CO2
 Values in shaded cells are calculated from measurements outside range of performance requirements and excluded from average

Values of d13VSMOW, d13SLAP, and d13LSG are expected to be different across the laboratories, but identical within any laboratory, since these samples are derived from the same laboratory CO2 (for Lab#5 and Lab#7, where different gases were used for LSG and water equilibration, only d13VSMOW and d13SLAP are expected to be equal).

Fit Coeff 1	-0.11	0.16	-0.01	0.21	-0.04	0.04	0.44	-0.11
Fit Coeff 2	0.06	0.09	0.02	0.11	0.03	0.02	0.31	0.03

Fit Coeff 1 is the difference between d13(VSMOW) and d13(SLAP). The sum of these for the four laboratories meeting performance criteria for these data is listed at right.

Fit Coeff 2 is the standard deviation between d13(VSMOW), d13(SLAP), and d13(LSG), except for Lab#5 and Lab#7, where d13(LSG) is excluded. The average standard deviation across the four laboratories meeting performance criteria for these data is listed at right.

APPENDIX 5:
Links to Current NIST Reports of Investigation for Reference Materials
Included in this Exercise

Waters

[Report of Investigation for RM 8535](#)

[Report of Investigation for RM 8537](#)

Carbonates

[Report of Investigation for RM 8543](#)

[Report of Investigation for RM 8544](#)

[Report of Investigation for RM 8545](#)

[Report of Investigation for RM \(8566\)*](#)

Carbon Dioxides

[Report of Investigation for RM 8562](#)

[Report of Investigation for RM 8563](#)

[Report of Investigation for RM 8564](#)

*Pending.