U. S. Department of the Interior
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Measurement of $\delta^{13}C$ and $\delta^{18}O$ Isotopic Ratios Of $CaCO_3$ using a Thermoquest Finnigan GasBench II Delta Plus XL Continuous Flow Isotope Ratio Mass Spectrometer with Application to Devils Hole Core DH-11 Calcite

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CONTENTS

ILLUSTRATIONS

APPENDIXES

CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
Length		
millimeter (mm)	0.03937	inch
centimeter (cm)	0.3937	inch
meter (m)	3.281	foot
Volume		
microliter (μl)	0.00006102	cubic inch
milliliter (mL) cubic centimeter (cc)	0.06102	cubic inch
Mass		
microgram (μg)	3.527×10^{-8}	ounce
gram (g)	0.03527	ounce
kilogram (kg)	2.205	pound avoirdupois
Mass Density		
gram per cubic centimeter (g/cc)	0.5780	ounce per cubic inch

Temperature in degrees Celsius (ºC) may be converted to degrees Fahrenheit (ºF) as follows:

$$ºF = (1.8 \times ºC) + 32$$

MEASUREMENT OF $\delta^{13}C$ AND $\delta^{18}O$ ISOTOPIC RATIOS OF $CACO_3$ USING A THERMOQUEST FINNIGAN GASBENCH II DELTA PLUS XL CONTINUOUS FLOW ISOTOPE RATIO MASS SPECTROMETER WITH APPLICATION TO DEVILS HOLE CORE DH-11 CALCITE.

by Kinga M. Revesz, Jurate M. Landwehr and Jerry Keybl

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ABSTRACT

A new method was developed to analyze the stable carbon and oxygen isotope ratios of small samples (400±20 μg) of calcium carbonate. This new method streamlines the classical phosphoric acid – calcium carbonate (H_3PO_4 – $CaCO_3$) reaction method by making use of a Thermoquest-Finnigan GasBench II preparation device and a Delta Plus XL continuous flow isotope ratio mass spectrometer. To obtain reproducible and accurate results, optimal conditions for the H_3PO_4 – $CaCO_3$ reaction had to be determined. At the acid-carbonate reaction temperature suggested by the equipment manufacturer, the oxygen isotope ratio results were unsatisfactory (standard deviation (σ) greater than 1.5 per mill), probably because of a secondary reaction. When the acid-carbonate reaction temperature was lowered to 26ºC and the reaction time was increased to 24 hours, the precision of the carbon and oxygen isotope ratios for duplicate analyses improved to 0.1 and 0.2 per mill, respectively.

The method was tested by analyzing calcite from Devils Hole, Nevada, which was formed by precipitation from ground water onto the walls of a sub-aqueous cavern during the last 500,000 years. Isotope-ratio values previously had been obtained by the classical method for Devils Hole core DH-11. The DH-11 core had been recently re-sampled, and isotope-ratio values were obtained using this new method. The results were comparable to those obtained by the classical method. The consistency of the isotopic results is such that an alignment offset could be identified in the re-sampled core material, a cutting error that was then independently confirmed. The reproducibility of the isotopic values is demonstrated by a correlation of approximately 0.96 for both isotopes, after correcting for an alignment offset. This result indicates that the new method is a viable alternative to the classical method. In particular, the new method requires less sample material permitting finer resolution and allows automation of some processes resulting in considerable timesavings.

INTRODUCTION

Calcium carbonate or calcite ($CaCO_3$) can be analyzed for the stable isotopes of carbon and oxygen to determine the ratios of the rare to the more common isotopes, respectively. The classical method used to obtain carbon and oxygen isotope ratios in calcite (McCrea, 1950) is labor intensive and requires relatively large sample sizes (20 mg). Samples are loaded in a y-shaped vessel with 100 percent phosphoric acid (2 ml) in one branch and the carbonate sample in the other. The vessel is evacuated on a vacuum line, and placed in a constant temperature bath

(25 ± 0.1ºC). When the temperature stabilizes, each vessel is oriented in such a way as to have the acid flow and react with the carbonate sample as:

$$CaCO_{3\,(s)} + H_3PO_{4\,(l)} \rightarrow CaHPO_{4\,(s)} + H_2O_{\,(l,\,g)} + CO_{2\,(g)} \qquad (1)$$

The reaction of acid with calcite produces solid calcium hydrogen phosphate, liquid water, and two gases, water vapor and carbon dioxide. The water is removed manually by cryogenic separation. First, both gases are frozen in liquid nitrogen. The frozen gases then are exposed to a dry ice slush, where the carbon dioxide sublimates and the water stays frozen. After two iterations of melting and then freezing of the gases, it is possible to remove the water vapor from the carbon dioxide. At this point, the carbon dioxide can be analyzed with a dual inlet isotope ratio mass spectrometer (DIIRMS).

A mass spectrometer is used to determine the ratio (R) of the heavy (rare) isotope to the light (abundant) isotope in a sample. The δ value or proportional difference from a standard is used almost exclusively in the Earth sciences for reporting stable isotope abundances and variations. Carbon and oxygen isotope data are reported as differences in parts per thousand (per mill or ‰) from their respective reference materials. The δ value is defined as

$$\delta_x = \left(\frac{R_x - R_{std}}{R_{std}} \right) 10^3, \qquad (2)$$

where R_x=(C^{13}/C^{12})$_x$ or (O^{18}/O^{16})$_x$ for the sample X, and R_{std} is the corresponding stable isotope ratio in the reference standard (Friedman and O'Neill, 1977). The δ values for the carbon isotope or $\delta^{13}C$ reported relative to Vienna Peedee belemnite [VPDB], are defined as $\delta^{13}C_{NBS19/VPDB}$ = +1.95 per mill (Hut, 1987). The δ values for the oxygen isotope or $\delta^{18}O$ are reported relative to Vienna Standard Mean Ocean Water [VSMOW] on a scale normalized to $\delta^{18}O$ of Standard Light Antarctic Precipitation [SLAP] = -55.5 per mill (Coplen, 1988).

The classical method (McCrea, 1950) requires a relatively large sample (20 mg) and each sample must be prepared by hand. The classical method was streamlined to make use of robotic technologies and a more sensitive continuous flow isotope ratio mass spectrometer (CFIRMS) that is presently available (Finnigan Delta XL). This new method uses only 400 µg of calcite or 2 percent of the sample required in the classical method. Also, only 10 percent of the acid previously required is used. To be viable, this new method should provide results that are similar in accuracy and precision to those of the classical method. The purpose of this report is to describe the development and application of this new method.

METHODOLOGY AND EQUIPMENT

The new method discussed here makes use of a continuous flow isotope ratio mass spectrometer (CFIRMS), the Thermoquest-Finnigan Delta Plus XL. Attached to this mass spectrometer is a preparation device (Thermoquest GasBench II) with a robotic sampling arm by which the sample ultimately is sent to the mass spectrometer (Fig. 1). However, the calcium carbonate samples first must be properly prepared.

The sample initially was dried in an oven at 90ºC overnight to prevent any moisture from reacting with carbon dioxide and exchanging an oxygen atom. This drying needed to be done only once, as long as the sample was kept in a tightly sealed container when not in use. The sample vessels, 12.5 x 100 mm borosilicate glass, also were dried in a 90°C oven for at least 24 hours. Once the vessels were removed from the oven, they were capped immediately to keep out the moisture. Each glass vessel was washed before reuse. Each set of vessels was rinsed eight times with tap water and once with de-ionized (DI) water. An ultrasonic bath then was filled with DI water and all of the vessels were submerged. The vessels were cleaned in the ultrasonic bath for 30 minutes, changing the water three times. The vessels then were removed, emptied and, dried as described previously.

Each dried sample was weighed on a microbalance in an aluminum boat with a target weight of 400 ± 20 μg. Each sample then was transferred quantitatively to a clean and dried sample vessel and capped with a rubber septum (Labco Limited, Pierceable Rubber Wad). The rubber septum retains an airtight seal after being punctured with a needle. A sample set, consisting of up to 94 vessels containing calcium carbonate, was loaded into the GasBench II auto sampler. For each sample in the set, two aliquots were run. The carbon and oxygen isotope ratios of these two aliquots were compared later to see if they were within the accepted range (0.1 and 0.2 per mill for $\delta^{13}C$ and $\delta^{18}O$, respectively); if not, additional aliquots were analyzed. Vessels containing one of three isotopically different kinds of reference materials also were interspaced among the samples. No less than one set of reference materials for every eight unknowns was analyzed. The weights of reference materials were in the same range as that of the samples.

After the set of samples and reference materials were assembled, vessels were loaded into the GasBench II tray. The GasBench II preparation device as well as CFIRMS were controlled by the Isotope Data (ISODAT) computer program. Sample information, including sample ID and weight, were added to the queue of the ISODAT program. Vessels containing acid also were added to the tray. While carbonate and acid were in the GasBench II, the tray was kept at a constant 26°C. This way the acid temperature was identical to that of the sample before it was added. The GasBench II then automatically flushed the samples with helium using the flushing needle to inject helium and displace the air contained above the samples. Helium is the carrier gas for the CFIRMS; it is inert and reacts with neither the sample nor the mass spectrometer. Helium has a mass (4), which is substantially different than the mass of CO_2 (44; 45; 46).

After the flushing process was complete, acid was added to the calcium carbonate. To prevent any oxygen atoms from exchanging with the carbon dioxide, only 100 percent phosphoric acid (1.906 g/cc) was used. A gastight syringe was used to transfer 0.1 ml of acid into each sample vessel. Care was taken to keep the septum acid free. The samples were left to react with the acid for 24 hours and the resulting gases were analyzed automatically over night in sequential sample order. The "method" in ISODAT was defined in such a way that each set of seven sample gas injections was bracketed by three reference gas injections, before and after each set.

The next day the sample vessels were removed and the data were transferred from ISODAT to a laboratory information management system (LIMS) (Coplen, 2000), where the final sample values were computed. For each sample, LIMS computed the δX value relative to a working standard, ($\delta^{13}C_{wstd}$ or $\delta^{18}O_{wstd}$) (equation 2), by defining the R_{std} as the average of the six

independently computed reference gas ratio that bracketed each sample set. A correction factor was applied to δX to obtain the $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VSMOW}$. This correction factor was computed as the linear fit between the analytic results for the three reference standard materials and their known reference values relative to VPDB and VSMOW, respectively. If the seven computed δ values of each of the two sample aliquots are not within the accepted ranges (0.1 and 0.2 per mill for $\delta^{13}C$ and $\delta^{18}O$, respectively), the samples were re-analyzed. A step-by-step procedure and a detailed set up for the $CaCO_3$ method in ISODAT are given in Appendixes A and B, respectively.

The reaction conditions ultimately chosen after a series of lab experiments were to maintain the acid reaction (1) at a constant temperature of 26ºC and (2) for a duration of 24 hours. Originally the samples were reacted at 65ºC, approximately the temperature suggested by the equipment manufacturer. At that temperature, reacted overnight, the carbon isotope ratios for the reference materials were reproducible and accurate, but the oxygen isotope ratios for the reference materials were neither accurate nor reproducible. Shortening the reaction time improved the reproducibility and accuracy of the oxygen isotope ratios of the working standard material (Figure 2). Using a lower reaction temperature (R.Yam, private communication, 2000) and a 24-hour reaction time allowed reproduction of isotope standards for both elements, carbon and oxygen (Figure 3). The fact that the length of the reaction affected oxygen isotope ratios, unlike the carbon isotope ratios, suggests that an exchange reaction for the oxygen isotope had been occurring during the overnight acid reaction period. Since the shortened reaction time of 1.5 hours gave acceptable results, this secondary reaction must have a kinetic component. Therefore, lowering the reaction temperature should inhibit or slow down this secondary reaction.

TESTING OF METHOD BY APPLICATION TO DEVILS HOLE CALCITE

Calcite from Devils Hole, Nevada was used to test this new method. Devils Hole is a tectonic cave formed in the discharge zone of a regional aquifer in south-central Nevada. Dense vein calcite has precipitated from the ground water onto the walls of this subaqueous cavern during the last 500,000 years (Winograd and others, 1992). Devils Hole Core DH-11 is a 36-cm long core taken from the wall of the cave at about 30 meters below the water table; it contains an approximately 500,000-year-old continuous record of the paleoclimate (Landwehr and others, 1997). The core was originally sampled along its length in approximately 1.27 mm intervals by milling. A new slab was cut from DH-11 and it was re-sampled in 1998 for other purposes. Material from the new slab was used for this study rather than the original material cut in 1997. This study analyzed material that had been identified as being re-sampled at distances of 165.7 mm to 266.0 mm from the free (outer) face of the core, which would correspond to precipitate from approximately 320 ka to 450 ka (thousands of years before present), respectively. The ratio of carbon isotopes (C^{13}/C^{12}) and of oxygen isotopes (O^{18}/O^{16}) are of interest for the study of global paleoclimatic conditions.

Calcite re-sampled from core DH-11 was analyzed by the new method. The analytical results, compiled into a data table organized by the reported re-sampling depth of each sample, are given in Appendix C. The stable isotope data plotted with the re-sampled depth is shown in Figure 4. An inverse relation results between the oxygen and carbon isotope ratio data, consistent with the pattern reported by Coplen and others (1994).

For a check of method consistency, three samples of the re-sampled material (at approximately 232, 233, and 234 mm) also were analyzed using the classical method. These data are shown in Figure 4 as stars and listed at the bottom of Appendix C. All results differ by less than 0.1 per mill and this corroborates the consistency of the two methods.

When the re-sampled series (filled symbols in Fig. 4 and 5) were compared with the original data (open symbols), two offsets that increased with depth were noted (Fig. 4). This observation was confirmed to accord with periodic re-positioning of the specimen during milling when it was observed to be slipping in the vise (A.C.Riggs, private communication, 2001). A mathematical correction to the recorded cutting depths was applied to accommodate these re-sampling conditions (Fig. 5).

When the results of the new method, with corrected sampling depths, are compared to the classical method (Fig. 5), it can be seen that the new method reproduced the classical method. The reproducibility of the isotopic values is demonstrated by a correlation of approximately 0.96 for both isotopes, after correcting for an alignment offset. Hence the new method can be used as an alternative to the classical method. However, care must be taken to check the precision of the standards, since reruns might be necessary. These additional analyses require time, but overall the automation of the GasBench II method results in considerable timesavings. The capability to make use of smaller sample sizes makes the GasBench II method superior to the classical method when sample amount is limited and/or finer sampling resolution is desirable.

SUMMARY

Calcium carbonate or calcite ($CaCO_3$) can be analyzed for the stable isotopes of carbon and oxygen. A new method was developed to analyze small samples (approximately 400 μg of calcium carbonate). The new method streamlines the classical H_3PO_4 – $CaCO_3$ reaction method by making use of a Thermoquest-Finnigan GasBench II preparation device and a Delta Plus XL continuous flow isotope ratio mass spectrometer. The method was tested by analyzing calcite from Devils Hole, Nevada core DH-11.

Results using the new GasBench II were comparable to the results obtained when the classical method was used. The advantages of the new method are that it requires less sample materials, making finer sampling resolution possible as well as automating several processes resulting in considerable time saving. These advantages make the GasBench II method a viable alternative to the classical method.

ACKNOWLEDGMENTS

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McCrea, J.M., 1950, On the isotopic chemistry of carbonates and a paleotemperature scale: J. Chem. Phys., 18, p. 849-857

Winograd, I.J., Landwehr, J.M., Ludwig, K.R., Coplen, T.B., Riggs, A.C., Szabo, B.J., Kolesar, P.T. and Revesz, K.M., 1992, Continuous 500,00-year climate record from vein calcite in Devils Hole, Nevada: Science, v. 258, p. 255-260.

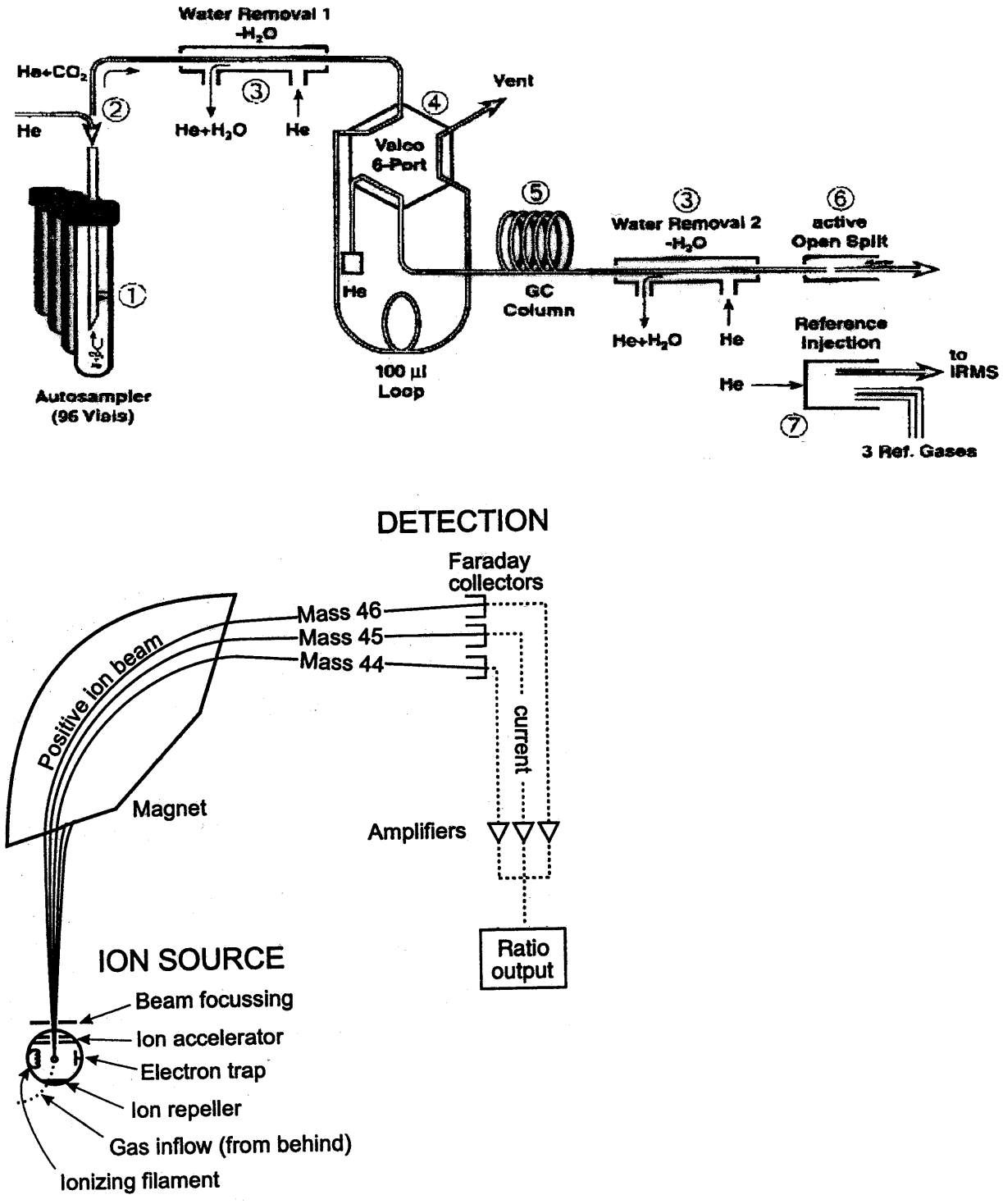

Figure 1. Schematic of GasBench II and Mass Spectrometer used for this study.

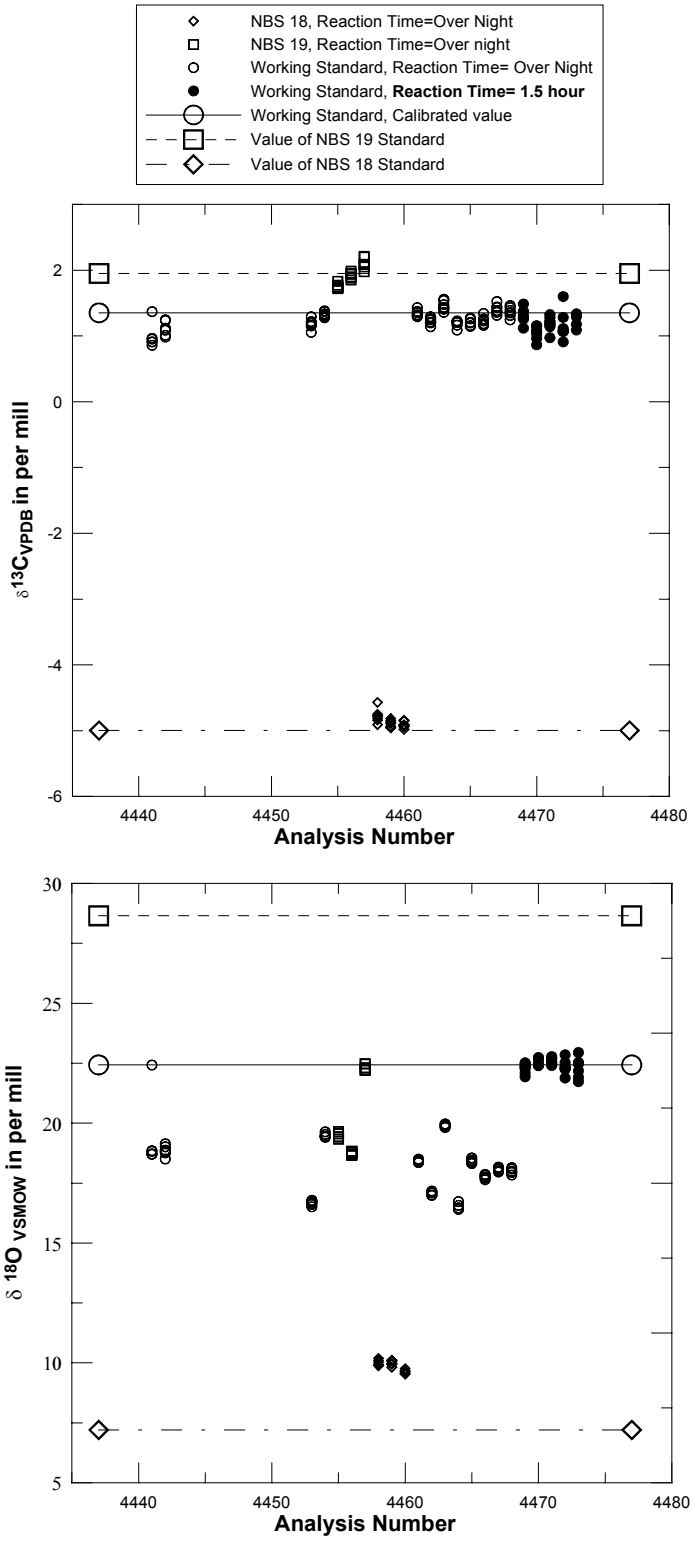

Figure 2. Precision and accuracy of standard reference materials using GasBench II at 65°C and two different reaction times (overnight and 1.5 hours). One analysis number represents 7 analyses of a sample.

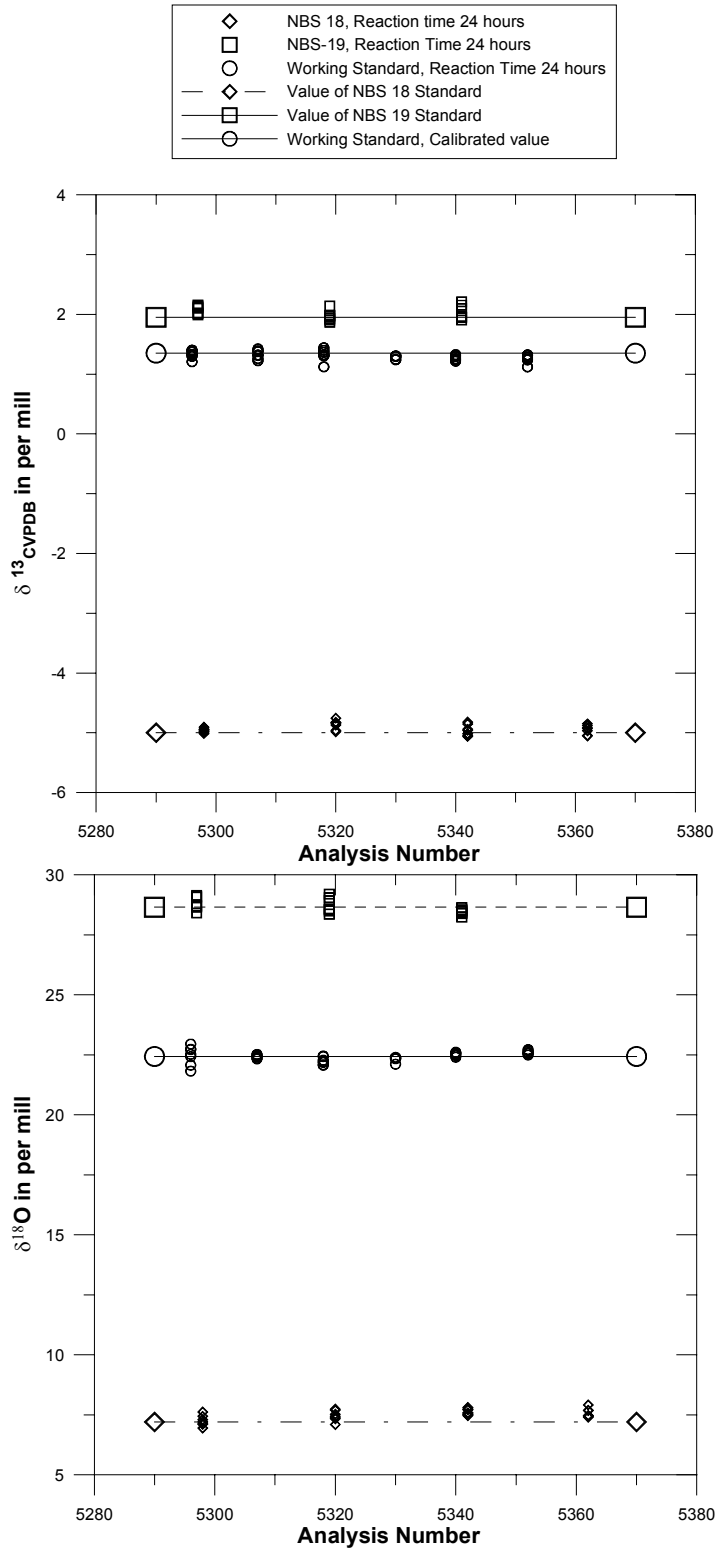

Figure 3. Precision and accuracy of standard reference material using GasBench II at 26°C and 24-hour reaction time. One analysis number represents 7 analyses of a sample.

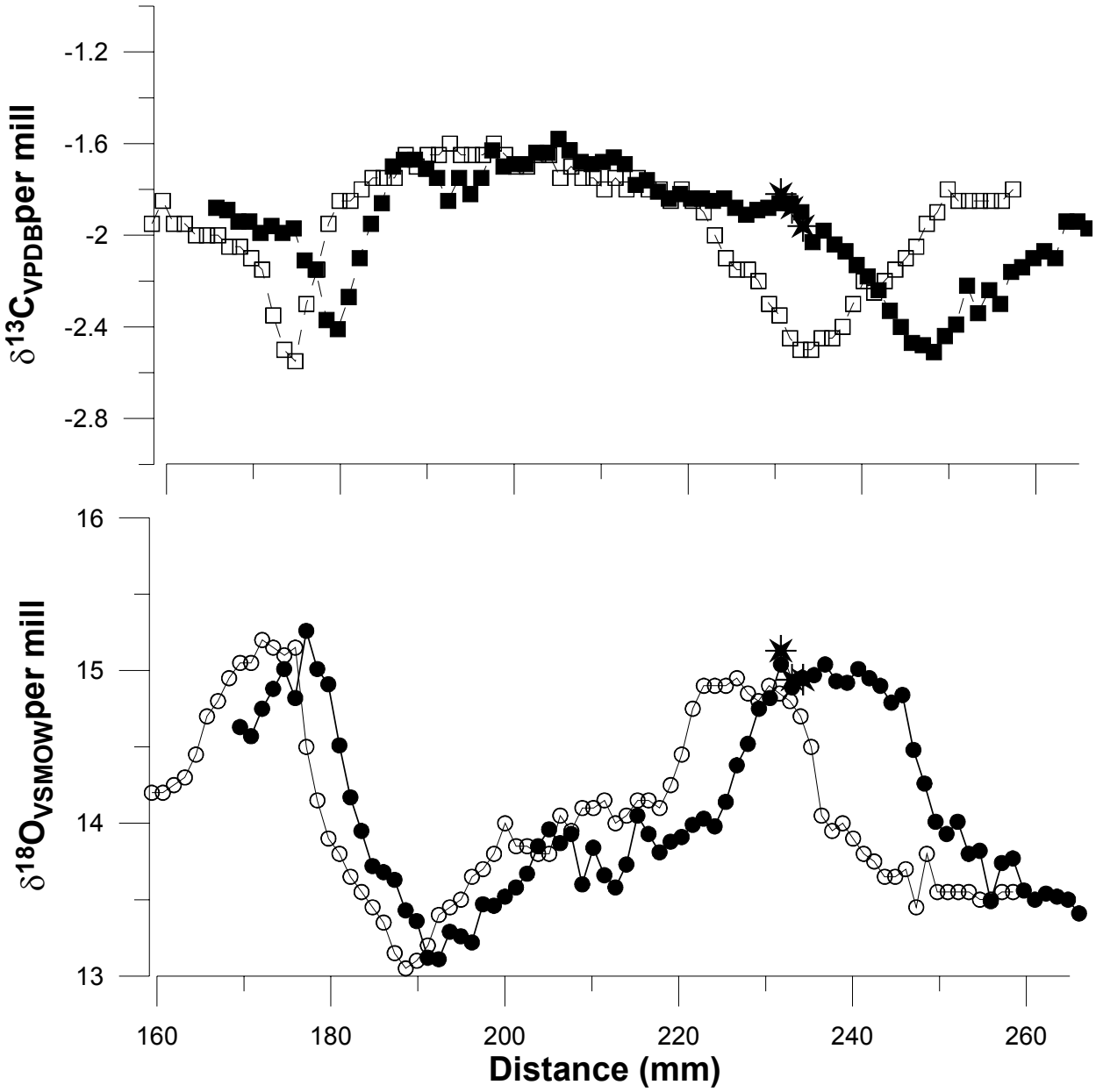

Figure 4. Stable carbon and oxygen ratio data profiles obtained by the GasBench II method for the re-sampled DH-11 core material compared to the original DH-11 analysis by the classical method. Filled symbols indicate data profiles of the re-sampled DH-11 core material obtained by the GasBench II method and star symbols indicate analysis of the same core by the classical method; open symbols indicate data profiles from the original DH-11 analysis obtained by the classical method, as reported by Landwehr and others (1997).

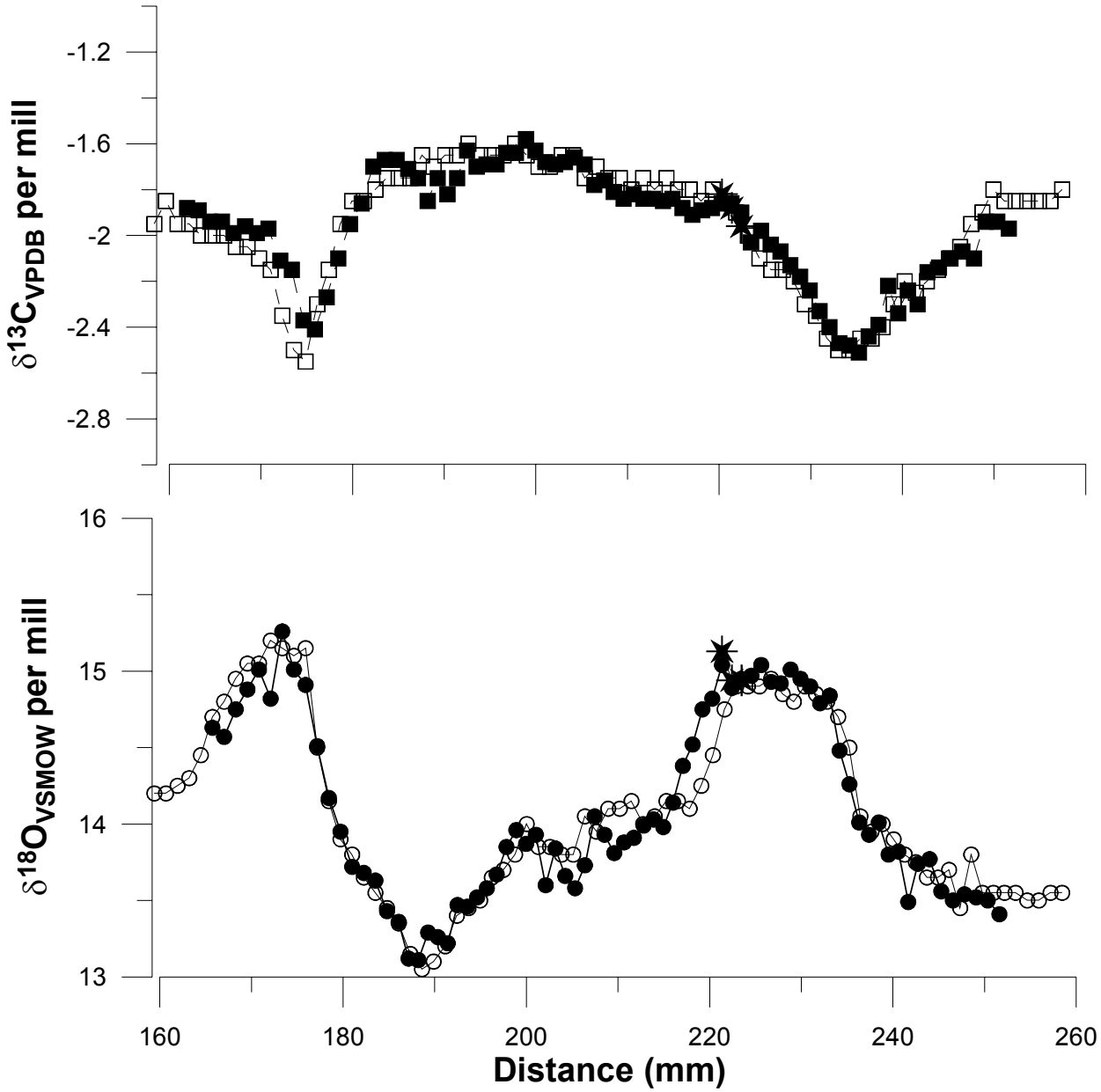

Figure 5. Stable carbon and oxygen ratio data profiles obtained by the GasBench II method for the re-sampled DH-11 core material, with appropriate sampling depth correction applied, compared to the original DH-11 analysis by the classical method. Filled symbols indicate data profiles of the re-sampled DH-11 core material obtained by the GasBench II method and star symbols indicate analysis of the same core by the classical method; open symbols indicate data profiles from the original DH-11 analysis obtained by the classical method, as reported by Landwehr and others (1997). The linear correlation between the data profiles for both isotopes is greater than 0.96.

APPENDIX A: COMPLETE STEP BY STEP PROCEDURE

Weighing and Storing Samples:

1. Samples should be dried overnight in a 90ºC oven and kept in sealed vessels.
2. Condition balance (this step should be done once a day):
   a. Place empty aluminum boat on balance and close door. Wait for reading to stabilize (the 'g' on the display appears). Tare the balance.
   b. Remove and replace boat and make sure the stabilized weight is 0.000 mg.
   c. Repeat these steps until the balance is stable.
3. Remove boat from balance, add sample and weigh the filled boat. Repeat until you have 400±20 µg.
4. Quantitatively transfer sample into a dried sample vessel and seal.
5. Mark sample ID and weight on the side of the vessel with a permanent marker.
6. Weigh boat again. It should read 0.000 mg. If it doesn't, there is a problem with the way in which the sample was weighed or transferred.
7. Repeat steps 2-5 for every sample.

Note:

1. Do not cross contaminate samples:
   a. Make sure aluminum boat always weighs 0.000 mg when empty.
   b. Make sure the spatula and sample area are cleaned using chem wipes.
2. Always allow balance to stabilize before removing boat.
3. Use the same boat until it becomes unusable.

Washing Sample Vessels:

1. Remove marker with chem wipe and Propanol (isopropyl alcohol).
2. Remove and dispose of the caps; place vessels in tray.
3. Rinse set of vessels 8 times with tap water and once with de-ionized (DI) water. Use mesh to hold vessels in place when emptying them.
4. Fill ultrasound with DI water. Place the vessels in the DI water.
5. Ultrasound the vessels for 30 minutes.
6. Remove the vessels and empty the water out of them. Place the vessels in a tray.
7. Dry vessels in a 90ºC oven for at least 24 hours.
8. Check the seals on the new caps and lay them out to cover the dried vessels with.
9. Remove vessels one by one from oven; cap dried vessels immediately to keep out moisture.

Loading Samples in Tray:

1. The needle assembly (sampling arm) must be moved out of the way by the GasBench II controller located on the left side of arm.
2. At job queue screen, press F1 (MENU).
3. Turn knob until SETUP is highlighted. Press 'Enter' (button is located inside the knob).
4. Turn knob until OBJECTS is highlighted. Press 'Enter.'
5. Turn knob until TRAYS is highlighted. Press 'Enter.'
6. Turn knob until 2ml-I is highlighted. Press 'Enter.'
7. Turn knob until OFFSET X (-44.2mm) is highlighted. Press 'Enter.'
8. Remove sample bath cover.
9. Load samples using the left upper port as 1. Note port, sample ID, and weight as the samples are entered. The sequence is loaded left to right, top to bottom.
10. Place vessels containing 100% pure phosphoric acid (H_3PO_4) into the last 3 ports.
11. Replace bath cover. (Make sure the hole for the cable is located on the backside of the cover.)

12. Press F4 (HOME) to return the sampling arm to its normal position.

Flush Samples:
1. Make sure that the flushing needle is in the GasBench II sampling arm.
2. Open the valve of the flushing helium tank. Check the flow of the GasBench II regulator marked "Ref 3." It should be set at 21 psi.
3. ISODAT Settings:
   a. Select GASBENCH from CONFIG column.
   b. Select "A-CON-B" from ENVIR. Column
   c. Select "2. SEQUENCE ACQ." (If the option is not visible, hit ALT-T.)
   d. Make sure TABLE NAME value is highlighted.
   e. Select TABLE DIR from status bar at bottom of screen.
   f. Select FLUSH from options and right-click it.
   g. Check to make sure START LINE and END LINE match what samples you have loaded.
   h. Click SAVE from status bar.
   i. Click MEASURE from status bar to begin flushing.

Add Sample Information to Queue:
1. Select GASBENCH from CONFIG column.
2. Select EDIT-B from ENVIR. Column.
3. Select 2. SEQUENCE EDITOR. If you do not see it, hit ALT-T.
4. Select CACO3.
5. Click EDIT from status bar.
6. Enter GasBench II Port # / GasBench II Method #
7. Enter Sample ID in SAMPLE IDENT field. Enter must be hit after every change in order for ISODAT to accept it.
8. Enter process File.
9. Enter the mass into the SAMPLE SIZE field.
10. Add any comments concerning the sample that you may have.
11. Click NEXT LINE from status bar for the next sample.
12. Repeat steps 6-9 for every sample.
13. When finished, click EXIT/SAVE from status bar.

Note:
The EDIT MASK and COPY MASK commands can be used to avoid typing repetitive data.

Add Acid:
1. Move sample arm out of the way (see **Loading Samples in Tray**, steps 2-7).
2. Place the gas tight syringe into the acid and suck up 0.1 ml of acid.
3. Remove the syringe from the acid and wipe the extra acid of the tip with a chem wipe.
4. Punch the syringe into the rubber septum of the sample vessels. Hold the plunger in place. It is best to punch the septum off center.
5. Expel the acid and wait 30 seconds to make sure that no acid remains on the needle. Remove the syringe.
6. Repeat steps 2-5 for each sample vessel in the set.
7. Press F4 (HOME) to return the sampling arm to its normal position.
8. Wait 24 hours before running the samples.

Run Samples:
1. Select GASBENCH from CONFIG column.
2. Select ACON-B from ENVIR. Column.
3. Select "2. SEQUENCE ACQ." If this option is not visible, hit ALT-T.

4. Make sure the TABLE NAME field is highlighted. Select TABLE DIR from status bar.
5. Select CACO3 and right click on it.
6. Change START LINE and END LINE to correspond to what samples will be run.
7. Select SAVE from the status bar.
8. Select MEASURE from the status bar.

Retrieve Data from ISODAT:

1. Select GASBENCH and EVAL-B from the CONIG AND ENVIR. Columns.
2. Select "1. OFFLINE EVALUATION." If this option is not visible, hit ALT-T.
3. Select Sort Index (default is Spec #).
4. Choose DIRECTORY from the status bar.
5. Tag all the runs using the TAG ALL command and parenthesis.
6. Select ONL-EDIT from the Screen. Column.
7. Page down to the fourth page.
8. Enter "NO" in the LIST TYPE field.
9. Enter "ALL" in the PEAK REPORT field.
10. Enter "a:\mmddyy.wks" in the FILE NAME field.
11. Enter "FORMAT1" in the LIST TYPE field.
12. Enter "LOT" in the FILETYPE field.
13. Choose EVAL.
14. When the exporting process is complete, choose EXIT.

Store Data in LIMS:

1. Open file in Excel. (*.wks file from floppy)
2. Select filter from the data menu. Filter runs 1, 2, 3, 11, 12, and 13.
3. Fill the R column with asterisks, once the runs are filtered.
4. Save the modified file.
5. Start LIMS.
6. Choose "Import Analysis."
7. Choose Mass Spec Delta-XL.
8. Click Import.
9. Select the file that will be imported.
10. Select columns F30 and F31. Check the boxes to import these two columns.
11. Click Import.

APPENDIX B: ISODAT "CACO3" METHOD

```
METHOD :  CACO3

>>> E X P E R I M E N T <<<

COMMENT
                    COMMENT                         :
GAS
                    GASNAME                         : CO2-CONF
                    CUP # 3                         : 44.0
                    CUP # 4                         : 45.0
                    CUP # 5                         : 46.0
                    RATIO 1 X/Y                     : 45.0  /  44.0
                    RATIO 2 X/Y                     : 46.0  /  44.0
CHANGEOVER
                    COV PORT #1                     : VAR. VOLUME 1
                    COV PORT #2                     : VAR. VOLUME 2
                    COV PORT #3                     :
                    COV PORT #4                     :
                    STANDARD PORT #                 : 7
                    SAMPLE PORT #                   : 5
MEASURE
                    ORDER                           : S
                    PEAKCENTER                      : YES
                    MASS                            : 45.0
                    STORAGE OFFSET TIME  [SEC]      : 10
                    ACQ. END TIME        [SEC]      : 1060
                    INTEGRATION TIME     [SEC]      : 0.250
PEAK DETECT
                    STARTING SLOPE     [mV/SEC]     : 0.400
                    ENDING SLOPE       [mV/SEC]     : 0.400
                    MIN. AMPLITUDE           [V]    : 0.100
PEAK CALCULATION
                          BACKGROUND TYPE    :  I
                            TYPE T STARTTIME:  20
                            TYPE T ENDTIME   :  30
                          SOURCE CALIBRATION:  NO
STANDARD PEAKS
                          1  :  140   DELTA 1 : 0.000    DELTA 2:   0.000
                          2  :  0     DELTA 1 : 0.000    DELTA 2:   0.000
                          3  :  0     DELTA 1 : 0.000    DELTA 2:   0.000
                          4  :  0     DELTA 1 : 0.000    DELTA 2:   0.000
                          5  :  0     DELTA 1 : 0.000    DELTA 2:   0.000

>>> P R O C E S S       <<<  MODE : GASBENCH II

      STD. MEASUREMENT [SEC]  VALCO [SEC]              SPLIT [SEC]
        ON          OFF          INJECT     LOAD        IN          OUT
    1:  30          50       1:  1          120      1: 1           0
    2:  80          100      2:  150        220      2: 0           0
    3:  130         150      3:  250        320      3: 0           0
    4:  0           0        4:  350        420      4: 0           0
    5:  0           0        5:  450        520      5: 0           0
    6:  0           0        6:  550        620      6: 0           0
    7:  0           0        7:  650        720      7: 0           0
    8:  0           0        8:  750        0        8: 0           0
    9:  0           0        9:  0          0        9: 0           0
      STD. MEASUREMENT [SEC]  VALCO [SEC]              SPLIT [SEC]
        ON          OFF          INJECT     LOAD        IN          OUT
   10: 950         970      10: 0          0        10:0           0
   11: 990         1010     11: 0          0        11:0           0
   12: 1020        1040     12: 0          0        12:0           0
   13: 0           0        13: 0          0        13:0           0
   14: 0           0        14: 0          0        14:0           0
   15: 0           0        15: 0          0        15:0           0
   16: 0           0        16: 0          0        16:0           0
   17: 0           0        17: 0          0        17:0           0
   18: 0           0        18: 0          0        18:0           0

>>> P 0 R M A T          <<< MODE: FORMAT

PRINTER
LIST TYPE              : FORMATI GRAPHICS              : NO
```

APPENDIX C: DATA TABULATION

OurLabID	Field ID	Resampling Depth		Corrected Depth	Isotopes (per mill)	
		inches	mm	mm	$\delta^{13}C$	$\delta^{18}O$
Run with new method						
C-10699	DH-11 6.50-6.55	6.525	165.735	161.935	-1.88	-
C-10700	DH-11 6.55-6.60	6.575	167.005	163.205	-1.89	-
C-10701	DH-11 6.60-6.65	6.625	168.275	164.475	-1.94	-
C-10702	DH-11 6.65-6.70	6.675	169.545	165.745	-1.94	14.63
C-10703	DH-11 6.70-7.75	6.725	170.815	167.015	-1.99	14.57
C-10704	DH-11 6.75-6.80	6.775	172.085	168.285	-1.96	14.75
C-10705	DH-11 6.80-8.85	6.825	173.355	169.555	-1.99	14.88
C-10706	DH-11 6.85-6.90	6.875	174.625	170.825	-1.97	15.01
C-10707	DH-11 6.90-6.95	6.925	175.895	172.095	-2.11	14.82
C-10708	DH-11 6.95-7.00	6.975	177.165	173.365	-2.15	15.26
C-10709	DH-11 7.00-7.05	7.025	178.435	174.635	-2.37	15.01
C-10710	DH-11 7.05-7.10	7.075	179.705	175.905	-2.41	14.91
C-10711	DH-11 7.10-7.15	7.125	180.975	177.175	-2.27	14.51
C-10712	DH-11 7.15-7.20	7.175	182.245	178.445	-2.10	14.17
C-10713	DH-11 7.20-7.25	7.225	183.515	179.715	-1.95	13.95
C-10714	DH-11 7.25-7.30	7.275	184.785	180.985	-1.86	13.72
C-10715	DH-11 7.30-7.35	7.325	186.055	182.255	-1.70	13.68
C-10716	DH-11 7.35-7.40	7.375	187.325	183.525	-1.67	13.63
C-10717	DH-11 7.40-7.45	7.425	188.595	184.795	-1.67	13.43
C-10718	DH-11 7.45-7.50	7.475	189.865	186.070	-1.71	13.36
C-10719	DH-11 7.50-7.55	7.525	191.135	187.139	-1.75	13.12
C-10720	DH-11 7.55-7.60	7.575	192.405	188.208	-1.85	13.11
C-10721	DH-11 7.60-7.65	7.625	193.675	189.277	-1.75	13.29
C-10722	DH-11 7.65-7.70	7.675	194.945	190.347	-1.82	13.26
C-10723	DH-11 7.70-7.75	7.725	196.215	191.416	-1.75	13.22
C-10724	DH-11 7.75-7.80	7.775	197.485	192.485	-1.63	13.47
C-10725	DH-11 7.80-7.85	7.825	198.755	193.554	-1.70	13.46
C-10726	DH-11 7.85-7.90	7.875	200.025	194.623	-1.69	13.52
C-10727	DH-11 7.90-7.95	7.925	201.295	195.692	-1.69	13.58
C-10728	DH-11 7.95-8.00	7.975	202.565	196.761	-1.64	13.67
C-10729	DH-11 8.00-8.05	8.025	203.835	197.830	-1.64	13.85
C-10730	DH-11 8.05-8.10	8.075	205.105	198.900	-1.58	13.96
C-10731	DH-11 8.10-8.15	8.125	206.375	199.969	-1.63	13.87
C-10732	DH-11 8.15-8.20	8.175	207.645	201.038	-1.68	13.93
C-10733	DH-11 8.20-8.25	8.225	208.915	202.107	-1.69	13.60
C-10734	DH-11 8.25-8.30	8.275	210.185	203.176	-1.68	13.84
C-10735	DH-11 8.30-8.35	8.325	211.455	204.245	-1.66	13.66
C-10736	DH-11 8.35-8.40	8.375	212.725	205.314	-1.69	13.58
C-10737	DH-11 8.40-8.45	8.425	213.995	206.383	-1.78	13.73
C-10738	DH-11 8.45-8.50	8.475	215.265	207.453	-1.76	14.05
C-10739	DH-11 8.50-8.55	8.525	216.535	208.522	-1.81	13.93
C-10740	DH-11 8.55-8.60	8.575	217.805	209.591	-1.84	13.81

OurLabID	Field ID	Resampling Depth		Corrected Depth	Isotopes (per mill)	
		inches	mm	mm	$\delta^{13}C$	$\delta^{18}O$
C-10741	DH-11 8.60-8.65	8.625	219.075	210.660	-1.82	13.88
C-10742	DH-11 8.65-8.70	8.675	220.345	211.729	-1.84	13.91
C-10743	DH-11 8.70-8.75	8.725	221.615	212.798	-1.84	13.99
C-10744	DH-11 8.75-8.80	8.775	222.885	213.867	-1.85	14.03
C-10745	DH-11 8.80-8.85	8.825	224.155	214.937	-1.84	13.98
C-10746	DH-11 8.85-8.90	8.875	225.425	216.006	-1.88	14.14
C-10747	DH-11 8.90-8.95	8.925	226.695	217.075	-1.91	14.38
C-10748	DH-11 8.95-9.00	8.975	227.965	218.144	-1.89	14.52
C-10476	DH-11 9.00-9.05	9.025	229.235	219.213	-1.88	14.75
C-10477	DH-11 9.05-9.10	9.075	230.505	220.282	-1.86	14.82
C-10478	DH-11 9.10-9.15	9.125	231.775	221.351	-1.86	15.04
C-10479	DH-11 9.15-9.20	9.175	233.045	222.420	-1.90	14.89
C-10480	DH-11 9.20-9.25	9.225	234.315	223.490	-2.03	14.95
C-10481	DH-11 9.25-9.30	9.275	235.585	224.559	-1.98	14.97
C-10482	DH-11 9.30-9.35	9.325	236.855	225.628	-2.04	15.04
C-10483	DH-11 9.35-9.40	9.375	238.125	226.697	-2.07	14.93
C-10484	DH-11 9.40-9.45	9.425	239.395	227.766	-2.13	14.92
C-10485	DH-11 9.45-9.50	9.475	240.665	228.835	-2.18	15.01
C-10486	DH-11 9.50-9.55	9.525	241.935	229.904	-2.24	14.95
C-10487	DH-11 9.55-9.60	9.575	243.205	230.973	-2.33	14.90
C-10488	DH-11 9.60-9.65	9.625	244.475	232.043	-2.40	14.79
C-10489	DH-11 9.65-9.70	9.675	245.745	233.112	-2.47	14.84
C-10490	DH-11 9.70-9.75	9.725	247.015	234.181	-2.48	14.48
C-10491	DH-11 9.75-9.80	9.775	248.285	235.250	-2.51	14.26
C-10492	DH-11 9.80-9.85	9.825	249.555	236.319	-2.44	14.01
C-10493	DH-11 9.85-9.90	9.875	250.825	237.388	-2.39	13.93
C-10494	DH-11 9.90-9.95	9.925	252.095	238.457	-2.22	14.01
C-10495	DH-11 9.95-10.00	9.975	253.365	239.527	-2.34	13.80
C-10496	DH-11 10.00-10.05	10.025	254.635	240.596	-2.24	13.82
C-10497	DH-11 10.05-10.10	10.075	255.905	241.665	-2.30	13.49
C-10498	DH-11 10.10-10.15	10.125	257.175	242.734	-2.16	13.74
C-10499	DH-11 10.15-10.20	10.175	258.445	244.000	-2.14	13.77
C-10500	DH-11 10 20-10.25	10.225	259.715	245.270	-2.10	13.56
C-10501	DH-11 10.25-10.30	10.275	260.985	246.540	-2.07	13.50
C-10502	DH-11 10.30-1035	10.325	262.255	247.810	-2.10	13.54
C-10503	DH-11 10.35-10.40	10.375	263.525	249.080	-1.94	13.52
C-10504	DH-11 10.40-10.45	10.425	264.795	250.350	-1.94	13.50
C-10505	DH-11 10.45-10.50	10.475	266.065	251.620	-1.97	13.41
Rerun with classical method						
C-10478	DH-11 9.10-9.15	9.125	231.775	221.351	-1.82	15.13
C-10479	DH-11 9.15-9.20	9.175	233.045	222.420	-1.88	14.94
C-10480	DH-11 9.20-9.25	9.225	234.315	223.490	-1.96	14.94