METHOD VALIDATION REPORT

Secondary (Lab) Standard Validation for the Analysis of Carbonate Samples Using the GasBench IRMS

Date: October 6, 2009

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SUMMARY

International Standards:	NBS19 - Limestone, RM8544 NBS18 - Calcite IAEA-CO-9, $BaCO_3$
Absolute Values (‰)	NBS19: $\delta^{13}C_{VPBD}$ = 1.95, $\delta^{18}O_{VPBD}$ = -2.2 NBS18: $\delta^{13}C_{VPBD}$ = -5.014, $\delta^{18}O_{VPBD}$ = -23.2 IAEA-CO-9: $\delta^{13}C_{VPBD}$ = -47.32, $\delta^{18}O_{VPBD}$ = -15.6
Lab Standards	$CaCO_3$-Merck: Lot B649459 544 Na_2CO_3-Fisher: Lot 946040 $SrCO_3$- J.T. Baker: Lot 1424 (7-19b) $CaCO_3$-Leco: Lot No. 1016
Experimentally Determined Values (‰)	**$\delta^{13}C(SrCO_3)$ $\delta^{13}C(Leco)$ n** $CaCO_3$-Merck: -42.98400 -42.99991 24 Na_2CO_3-Fisher: -1.91534 -1.92850 24 $SrCO_3$- J.T. Baker: -4.68729 -4.70063 30 $CaCO_3$-Leco: -15.54381 -15.55790 24 **$\delta^{18}O(SrCO_3)$ $\delta^{18}O(Leco)$ n** $CaCO_3$-Merck: -17.46185 -17.45439 24 Na_2CO_3-Fisher: -17.87215 -17.86338 24 $SrCO_3$- J.T. Baker: -13.96552 -13.97135 30 $CaCO_3$-Leco: -21.31081 -21.28807 24 Note: SrCO3 and Leco were different std. curves used to discern the above experimentally determined values.

Standard Target Weights:	NBS19-Limestone: 150 - 225 µg NBS18-Calcite: 150 -225 µg IAEA-CO-9, $BaCO_3$: 350 – 450 µg $CaCO_3$-Merck: 175 – 275 µg Na_2CO_3-Fisher: 150 – 250 µg $SrCO_3$- J.T. Baker: 300 – 400 µg $CaCO_3$-Leco: 175 – 275 µg
Sample Preparation:	Weigh samples and standards. Carefully transfer sample to exetainer vials. Seal vials with blue, 1 mm drilled cap with new septa. Tap vial a few times, visually inspect to verify sample powder is not stuck to walls of the vial. Place vials in sample tray, tray should be set to 73°C. Instrument configuration: GasBench+PAL Flush Fill vials with Helium (T-valve towards the Gas Bench). Insert Flush Fill (FF) needles into the PAL Autosampler. CO_3 FF Method: Vial_Flush_6min.met CO_3 FF Sequence: CO3_FlushFill_6min.seq He FF rate: 125ml/min, verify at FF needle vent after FF sequence has been initiated and needle is in vial.
Acid Dosing:	Calibration: 6 - 7 strokes per drop (in Isodat). Analysis: 10 forward, 2 reverse drops (in the method) Reaction time: Approximately 60 minutes. Check alignment of acid syringe, needle must NOT make contact with vial cap. CO_3 analysis method controls acid dosing parameters. Set T-valve towards back wall (middle position). Analysis Methods: Carb_100uL_Loop&Sample&Acid_(CO_2).met Carb_100uL_Loop&Sample&No_Acid_(CO_2).met CO_3 Sequence: CO_3_Acid_Samples.seq

Instrument Conditions during Sample Analysis:	Reference Gas: CO_2 (Ref Gas 1) Instrument configuration: GasBench+PAL+Acidpump Fill acid vial in sample block with H_3PO_4. He pressure: 13–14 psi (at GasBench gauge) He pressure: 50 psi (at Tank regulator) Sample block temp: 73°C Capillary Column temp: 70°C Use CO_2_GB_Tune file, auto-tune on CO_2 reference gas. On-Off Method: CO2_On-Off.met (St.Dev. < 0.05) Linearity: CO2_On-Off.met (Regression < 0.06 with increasing pressure)
Instruments:	Thermo Delta V Advantage IRMS ThermoFinnigan Gas Bench II Sartorious Model CP2P, S/N 19502516 micro-balance

Inter-assay Precision (CV) and Accuracy (Acc)				
	$\delta^{13}C$ Precision and Accuracy			
		$\delta^{13}C(SrCO_3)$	**$\delta^{13}C(Leco)$**	**n**
	$BaCO_3$,IAEA-CO-9:			
	% CV	0.44	0.46	24
	% Acc	99.85	99.89	
	NBS-18, Calcite:			
	% CV	2.47	2.59	24
	% Acc	101.82	102.09	
	NBS-19, $CaCO_3$:			
	% CV	5.12	5.95	21
	% Acc	97.81	97.15	
	$CaCO_3$-Merck:			
	% CV	0.23	0.24	24
	% Acc	100.17	100.21	
	Na_2CO_3-Fisher:			
	% CV	7.25	7.35	24
	% Acc	102.23	102.94	
	$SrCO_3$- J.T. Baker:			
	% CV	1.75	1.98	30
	% Acc	99.12	99.40	
	$CaCO_3$-Leco:			
	% CV	0.53	0.52	24
	% Acc	99.43	99.52	
	$\delta^{18}O$ Precision and Accuracy			
		$\delta^{18}O(SrCO_3)$	**$\delta^{18}O(Leco)$**	**n**
	$BaCO_3$,IAEA-CO-9:			
	% CV	0.45	0.41	24
	% Acc	100.16	100.16	
	NBS-18, Calcite:			
	% CV	0.48	0.27	24
	% Acc	102.75	102.61	
	NBS-19, $CaCO_3$:			
	% CV	10.47	4.20	21
	% Acc	94.73	97.14	

Inter-assay Precision (CV) and Accuracy (Acc)	**$\delta^{18}O$ Precision and Accuracy (cont.)**		
	$\delta^{18}O(SrCO_3)$	**$\delta^{18}O$(Leco)**	**n**
$CaCO_3$-Merck:			
% CV	0.32	0.32	24
% Acc	100.46	100.42	
Na_2CO_3-Fisher:			
% CV	0.24	0.24	24
% Acc	99.45	99.41	
$SrCO_3$- J.T. Baker:			
% CV	0.49	0.63	30
% Acc	99.99	100.04	
$CaCO_3$-Leco:			
% CV	0.52	0.38	24
% Acc	100.14	100.04	

SIGNATURE PAGE

Secondary (Lab) Standard Validation for the Analysis of Carbonate Samples Using the GasBench IRMS

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION

This report describes the qualification process for carbonate laboratory standards as well as the analysis methods for carbonate analysis of $\delta^{13}C$ and $\delta^{18}O$ using the automated Gas Bench-Acid Dosing technique. Various carbonates ($CaCO_3$, K_2CO_3, $SrCO_3$, and Na_2CO_3) were sampled to be evaluated as possible laboratory (secondary) standards. Three international (primary) standards were included in the analyses, they are NBS-18 Calcite, NBS-19 Limestone, and IAEA-CO-9 Barium Carbonate. The goal of the analysis was to identify the laboratory standards which were most stable and encompassed the $\delta^{13}C$ and $\delta^{18}O$ ranges of the field samples submitted for analysis. The Lab Standards identified in the Summary section of this report fulfilled these requirements.

2. EXPERIMENTAL

2.1. CHEMICALS AND MATERIALS

Six carbonate samples were chosen for this laboratory (secondary) standard determination experiment, as well as the three international (or primary) standards. The six laboratory standard candidates are as follows:

1. $SrCO_3$ – J.T Baker Lot 1424, 7-19b
2. Na_2CO_3 – Fisher Lot 946040 S263-500
3. $CaCO_3$ – Fisher Lot 735383
4. K_2CO_3 – Baker Lot 806353 Food grade
5. $CaCO_3$ – Leco Lot No. 1016
6. $CaCO_3$ – Merck Lot B649459 544

The three international standards are as follows:

1. $BaCO_3$ IAEA-CO-9
2. NBS-18 Calcite
3. NBS-19 Limestone

The acid used for this procedure is Ortho-Phosphoric Acid 99% (H_3PO_4), Fluka 79622, Lot 1260282 42206382. This acid was included with the GasBench Instrumentation package. For this experiment the acid was taken straight from the bottle and placed into a sample vial which contained the acid dosing tube attached to the vial cap (there was no other acid preparation for this analysis). The acid needs to be at an elevated temperature (~73°C) for the analysis, so the acid vial was placed in position 12 of the heated sample block, this keeps the acid at the proper temperature for the duration of the analysis.

Capillary Column – Varian PN: CP7551, PLOT Fused Silica, CP-PoraPLOT Q, length - 27.5 meter (incl. 2.5 m particle trap), (0.32 mm I.D., 0.45 mm O.D., 10 mm film thickness).
Exetainer Vials – 12 mL Borosilicate, obtained from LabConco with 1 mm oversize (lab drilled) blue vial caps and disposable septa.
Valco Sample Loop – 100 µL
He Gas - Grade 5.0 (50 psi tank gauge, 13-14 psi GasBench gauge)

2.2. IRMS AND GASBENCH INSTRUMENTATION

The IRMS instrument is a Thermo Scientific Delta V Advantage along with a ThermoFinnigan GasBench III and CTC Analytics PAL autosampler system. (The GasBench unit comes with a self-contained continuous flow interface.) The acid pump is a FMI (Fluid Metering, Inc) Micro-π petter, and the balance is a Sartorius Model CP2P, S/N 19502516 micro-balance. The Sartorius micro-balance had been calibrated April 14, 2009 by Precision Scale and Balance (calibration is performed annually).

Data Acquisition System: Isodat 2.5 Gas Isotope Ratio M.S. Software

a. Acquisition - Used for running the analysis (acquiring data).
b. Workspace – Used for analysis setup, methods and sequence development, and data review.
c. Instrument Control – Used to monitor and control various aspects of the instrument, it is best not to use this when in Acquisition mode.

2.3. SAMPLE PREPARATION AND ANALYSIS PROCEDURE

Each of the three days of analyses for this validation consisted of 71 samples (including acid-blanks).
Seventy-one clean borosilicate Exetainer vials, along with 71 blue vial caps (custom drilled 1mm oversize) and new septa were placed in the vial prep holder and identified.
Target weights were determined for sample types by calculating the weight percent CO_3 per sample.
A CO_3 analysis worksheet which identified the testing protocol and target weights was created to record the actual weights. Target weights for this analysis were determined to be between 150 µg and 360 µg.
Note: During the first three analyses some samples were intentionally weighed out to two to four times over the target weights. This was done to determine the effect of the GasBench auto-diluter feature on the sample data. There was no statistical difference noted between data with the auto-diluter and data without the auto-diluter.
The carbonate samples were weighed using a small piece of weighing paper (cut a piece of weighing paper into 4 or 6 rectangular sections).
Place the paper on the balance and depress the tare button, wait a few seconds for the balance to stabilize.
Remove the paper.
Using the sample weighing tools and apparatus, carefully place some sample onto the paper.
Place the paper on the balance, slide the side door closed and allow the reading to stabilize.
If the weight is acceptable, record the sample weight on the analysis form, and then open the side door and carefully remove the paper with the sample.
Take the appropriate sample vial and slide the entire sample off the paper into the vial. Tap the sample vial on the table a few times, visually verify that the entire sample has fallen to the bottom of the vial (sometimes sample will stick to the sides of the vial, this is unacceptable).
Securely attach a sample cap with new septa onto the vial (to reduce the possibility of the acid needle being broken on a vial cap, use the blue caps which have been drilled out 1mm oversize).

Place the vial back into the tray.
Continue until all samples are weighed.
Place the sample vials into the heated (73°C) sample block, be sure to follow the sample tray layout to keep the samples in order.
Due to the acid dosing syringe and sampling needle arrangement of the PAL Autosampler, samples are acid dosed and analyzed in columns of four.
This arrangement allows for the approximately 60 minute reaction time for the acid and carbonate sample.
When the sample block is loaded, place the cover on it and secure the top to the base with the screw.
Each sample vial must be flush-filled with Helium before the analysis.
Attach the two flush-fill needles to the PAL autosampler.
Turn the T-valve so it points towards the GasBench.
In Isodat Acquisition, verify the configuration is for GasBench+PAL, click the mouse on the gasbench@flush-fill button in the GasBench area, this will purge the He flush-fill line.
Allow the He line to purge for at least 15 minutes.
Use the *CO3_FlushFill_6min.seq* as a template (in Workspace), create a flush-fill sequence for the appropriate number of samples.
Ensure the use of an appropriate AS Method, Internal No 1, (A200S-1) 6 injections of 61 seconds each. (See Figure 1)
Go to Acquisition and start the flush-fill sequence just created.
Identify the folder for the data with the date and type of analysis.
Once started, verify the flush-fill flow rate by placing the flow meter inlet onto the vent tube of the flush-fill needle (check this on both needles!), the flow rate should be ~ 125 mL/min.
If the flow rate is not correct, stop the sequence, identify and fix the problem.
If the flow rate is correct, continue with the sequence, this can be left to run overnight.
When the Helium flush-fill has been completed, turn the T-valve back 90° to point to the back wall and shut off the gas.
Remove both flush-fill needles from the PAL autosampler.
Attach the Sampling Needle to the left position on the PAL autosampler.
Change the instrument configuration to GasBench+PAL+AcidPump.
Before attaching the acid dosing needle, the acid pump needs to be primed and calibrated.
Carefully insert the acid dosing needle into a septum on an empty vial.
Turn the volume control ring counter-clockwise to increase the flow of acid at the needle tip.
Depress the manual controller switch until acid is expelled from the needle tip consistently (this could be 30 -100 or more clicks).
Slowly adjust the volume control ring clockwise to lessen the flow, check the number of clicks needed to dispense one drop of acid.
Adjust the ring to get six (or seven) clicks per acid drop (the manual indicates 10 clicks/drop, this was found to not work as well as 6 clicks/drop).
Right click on the Acid Pump – Direction area of the screen, "calibrate…" comes up, click it and type in the number of clicks/drop, click OK.
The acid pump is now calibrated.
The acid dosing needle attaches to the right side position of the PAL autosampler.
IMPORTANT: Be very careful with the alignment of the acid dosing needle, it is very thin and

can be broken very easily if it contacts the side of a sample vial. This is the reason for using the blue vial caps which have been drilled out 1mm oversize.

Open Instrument Control software, check and record the MS pressure.
Open the GasBench inlet needle valve on the IRMS.
Wait a few minutes for the pressure to stabilize, and record the pressure.
Turn on the filament.
Monitor m/z 18 (H_2O) on cup 3. The m/z 18 signal should drop below 1000 mV within 1 – 2 hours of turning on the filament.
When the m/z 18 signal is below 1000 mV, perform on-off and linearity analysis using CO_2 as the reference gas (Ref Gas 1). (13C - On-off: st.dev. < 0.06%, Linearity: regression < 0.06% with increasing pressure. 18O - On-off: st.dev. < 0.08%, Linearity: regression < 0.08% with increasing pressure.) (see Figures 7 and 8)
Adjust the CO2 reference gas to give a reference peak (m/z 44, cup 2) signal of between 7000 and 8000 mV. (m/z 45 ~ 8500 mV, m/z 46 ~ 10,000 mV)
Create, identify, and save a new CO3 Analysis sequence using the file *CO3_Acid_Samples.seq* as a template (see Figure 6).
Note: The sequence uses two similar method files which control the acid pump, reference gas injections, sample gas injections, peak identification, and evaluation information. These two method files are identified as:

1. Carb_100uL_Loop&Sample&Acid_(CO2).met
2. Carb_100uL_Loop&Sample&No_Acid_(CO2).met

The first method is used for the majority of the samples in the sequence. The second method is used when there is no sample vial on the right side of the vial being sampled, this method prevents acid from being dosed into the empty areas of the sample block (see Figures 2 – 5).
Ensure the correct autosampler method is entered in the sequence, Internal No. 9 (A200S-9) 11 injections of 59 sec. each. (See Figure 1)
Check sample vial placement in the sample block versus the block location number in the sequence file (sample location is irrelevant for the Flush-Fill sequence; however, it is critical for the analysis sequence!).
Before a sequence is started it is a good idea to re-boot the computer, close all programs and click restart.
When the system is back on-line, open Isodat Acquisition, and Isodat Workspace.
In Acquisition, check and record mass spectrometer pressure, the CO_2, N_2, H_2, m/z 18 (cup 3), m/z 32 (cup 3), and m/z 40 (cup 3) intensities.
Check and verify the system is ready for analysis, i.e. check Helium tank, pressures, column temp, T-valve position, alignment of syringes, acid quantity, vial location and identification, etc.
Verify the instrument configuration is GasBench+PAL+AcidPump.
Call up the sequence created earlier for the analysis.
Verify that the correct sequence has been selected and double check the information.
When all is correct, click “Start”.
Identify the folder in which the data files are to be stored (typically use CO3 followed by an underscore and then the analysis date).
Next choose how to identify the data files.
Un-check the “Auto Enum” button.

Click “Ok”.
The sequence should begin.
Monitor the first few samples to make sure the instrument, PAL, acid pump, etc, are performing properly.
Depending on the number of samples, the sequence can continue for more than 20 hours.
Continue to check the progress and status of the analysis.
Completed files can be reviewed in Isodat Workspace…\Results\filename. (see Figures 9 – 11 for example chromatograms for a blank, a primary standard, and a sample)
When the analysis is complete, review the files in Workspace to verify all samples were properly analyzed.
It is useful to record any anomalous findings or notes on the analysis on the analysis worksheet.
Print the data files in Workspace.
Re-process the data files using the export file *GB_CO3_Export.wke,* this will put the data into EXCEL format (see Figure 12).
Transfer the re-processed data via an appropriate technique to another computer for statistical analysis.
First copy the data into a new worksheet.
Clean up the spreadsheet, set significant figures, alignments, headings, etc, to make the spreadsheet easier to handle and interpret.
Sort on “Peak No.” to separate out the reference peaks.
Cut and paste the reference peak data into a new worksheet.
After the reference peaks have been removed, sort on the sample ID.
Create a calibration curve for $\delta^{13}C$ and $\delta^{18}O$ using the three primary standards, plot the known values vs. the IRMS determined values.
Plot the trend line, the equation of the trend line is the regression formula used to determine the corrected sample values.
Use these curves to determine the corrected sample values.
Perform statistical analysis (mean, standard deviation, accuracy, and %CV) on all the peaks acquired for each sample type. This is the inter-statistical analysis.
Next, perform the same statistical analysis on each individual samples peaks of each sample type. This is the intra-statistical analysis.
Finally, the statistical data from these three analyses were compiled and analyzed

2.4. CARBONATE STANDARD VALIDATION DATA

The Excel files used for this validation can be found on the network, the path is Campus on ESS P:\Instrumentation\Geosciences\Data\Thermo_IRMS\GasBench\Carbonate Analysis\(file names). The file names and contents are listed below:

1. CO3_050609.xlxs – Two primary standards used (NBS-19 and $BaCO_3$).
2. CO3_051209.xlxs – Two primary standards used (NBS-19 and $BaCO_3$).
3. CO3_051909.xlxs – Two primary standards used (NBS-19 and $BaCO_3$).
4. Primary_Standards_04009_to_051909.xlxs – Combined data from three prior runs to determine laboratory standard delta values (‰).
5. CO3_060109.xlxs – Accuracy and precision analysis, three primary standards. Status – accepted.

6. CO3_060509.xlxs – Accuracy and precision analysis, three primary standards. Status – accepted.
7. CO3_061009.xlxs – Accuracy and precision analysis, three primary standards. Status – accepted.
8. Sec to Prim CO3 Standards_060109_to_061009.xlxs – Combined data from previous three analyses. Accuracy and precision analysis of the three analyses. Read-back determination of primary standards using secondary standards. Status - accepted.

The first four files were used to determine values for the carbonate lab samples by creating a standard curve using two primary standards which were analyzed along with the carbonate samples. The %CV and % accuracy of the primary standards for these three analyses are:

Average %CV of Known Delta Value			
	n	**$\delta^{13}C$**	**$\delta^{18}O$**
NBS-19	16	3.85	4.78
$BaCO_3$	16	0.16	0.54

Average % Accuracy of Known Delta Values			
	n	**$\delta^{13}C$**	**$\delta^{18}O$**
NBS-19	16	98.65	101.20
$BaCO_3$	16	100.08	99.76

This analysis determined which carbonate samples would serve as the best potential secondary standards to be used for subsequent carbonate analyses, and also to verify the proper sample weights. To determine the effect of the diluter on the data, a number of samples were purposely analyzed at two to four times their target weights, this typically activated the diluter. There was no difference noted for the Delta values of sample data acquired with the diluter and data acquired without the diluter. The following is a summary of the results

1. Secondary Standards for $\delta^{13}C$*:
   a. $CaCO_3$-Merck: $\delta^{13}C$ = -42.91009‰, $\delta^{18}O$ = -17.38127‰
   b. Na_2CO_3-Fisher: $\delta^{13}C$ = -1.87349‰, $\delta^{18}O$ = -17.97011‰

*Note: The $\delta^{13}C$ spread (-42.91 to -1.87) for these two secondary standards is acceptable, the spread for $\delta^{18}O$ (-17.38 to -17.97) is not. Another secondary standard will need to be used to accurately provide $\delta^{18}O$ data.

2. Potential Secondary Standards for $\delta^{18}O$:
   a. $CaCO_3$-Leco: $\delta^{13}C$ = -15.6337‰, $\delta^{18}O$ = -21.28028‰
   b. $SrCO_3$-Baker: $\delta^{13}C$ = -4.7288‰, $\delta^{18}O$ = -13.96625‰

Two possible methods for $\delta^{18}O$ analysis were identified:

1. Use three secondary standards for an analysis: $CaCO_3$-Merck and Na_2CO_3 for $\delta^{13}C$, and the addition of either $SrCO_3$ or $CaCO_3$-Leco, the choice of which secondary standard to use would be made based on the estimate of the $\delta^{18}O$ value of the samples to be analyzed.
2. Use $SrCO_3$ in place of Na_2CO_3 and use two secondary standards for an analysis, this will not provide as wide a spread for $\delta^{13}C$ as the Na_2CO_3, but would give a better $\delta^{18}O$ spread.

The next four files were used to determine the accuracy and precision of the data using the values for the secondary carbonate standards determined in the first four files. All data from the three analysis files were subjected to two regression analyses using three secondary standards. The first regression used $CaCO_3$-Merck, Na_2CO_3, and $SrCO_3$ as standards, the second regression used $CaCO_3$-Merck, Na_2CO_3, and $CaCO_3$-Leco as standards. The statistics for each of these three files (CO3_060109.xlsx, CO3_060509.xlxs, and CO3_061009.xlxs) are provided in Tables 1, 2 & 3. The fourth file (Sec to Prim CO3 Standards_060109_to_061009.xlxs) combined the data from these three files. The overall data was then subjected to the same statistical analysis as the individual analysis files. As a final check, the primary standard values were back-calculated using the regression provided by the secondary standards. This data is provided in Table 4. Tables 5 and 6 summarize the $\delta^{13}C$ standards in chart form in order of increasing $\delta^{13}C$ and Tables 7 and 8 summarize the $\delta^{18}O$ standards in chart form in order of increasing $\delta^{18}O$. Table 9 averages the %Accuracy and %CV data from all three runs for the secondary standards, primary standards (read-back analysis), as well the combination of all standards.

Table 1:

File Name: CO3_060109.XLSX

Standards Statistics $CaCO_3$ and Na_2CO_3 regression				
Secondary	**$\delta^{13}C$ Regression**	**$\delta^{18}O$ Regression**		
$SrCO_3$	y = 1.0067x - 0.3788	y = 1.0612x - 0.3759		
Leco	y = 1.0076x - 0.3662	y = 1.0392x - 0.7266		
$CaCO_3$ Merck	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-43.02285	-43.04838	-17.45096	-17.44767
std dev	0.12529	0.12540	0.07483	0.07328
%CV	0.29	0.29	0.43	0.42
%Acc	100.26	100.32	100.40	100.38
n	5	5	5	5
$\delta^{18}O$	-17.38127	-17.38127	-17.38127	-17.38127
$\delta^{13}C$	-42.91009	-42.91009	-42.91009	-42.91009
Na_2CO_3	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-1.81785	-1.80654	-17.86205	-17.85024
std dev	0.05599	0.05604	0.05481	0.05368
%CV	3.08	3.10	0.31	0.30
%Acc	97.03	96.43	99.40	99.33
n	5	5	5	5
$\delta^{18}O$	-17.97011	-17.97011	-17.97011	-17.97011

$\delta^{13}C$	-1.87349	-1.87349	-1.87349	-1.87349
$SrCO_3$	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-4.62135	-4.61254	-13.96430	-14.03329
std dev	0.08932	0.08940	0.08522	0.08345
%CV	1.93	1.94	0.61	0.59
%Acc	97.73	97.54	99.99	100.48
n	7	7	7	7
$\delta^{18}O$	-13.96625	-13.96625	-13.96625	-13.96625
$\delta^{13}C$	-4.7288	-4.7288	-4.7288	-4.7288
Leco	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-15.54291	-15.54386	-21.41471	-21.32925
std dev	0.10326	0.10335	0.13447	0.13168
%CV	0.66	0.66	0.63	0.62
%Acc	99.42	99.43	100.63	100.23
n	5	5	5	5
$\delta^{18}O$	-21.28028	-21.28028	-21.28028	-21.28028
$\delta^{13}C$	-15.6337	-15.6337	-15.6337	-15.6337

File Name:
CO3_060109.XLSX

Standards Statistics Primary				
NBS-19	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	2.00505	2.01978	-1.88669	-2.20607
std dev	0.10645	0.10655	0.10580	0.10361
%CV	5.31	5.28	5.61	4.70
%Acc	102.82	103.58	85.76	100.28
n	8	8	8	8
$\delta^{18}O_{VPDB}$	-2.2	-2.2	-2.2	-2.2
$\delta^{13}C_{VPDB}$	1.95	1.95	1.95	1.95
$BaCO_3$	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-47.40679	-47.43623	-15.58360	-15.61902
std dev	0.10558	0.10568	0.07751	0.07590
%CV	0.22	0.22	0.50	0.49
%Acc	100.18	100.25	99.89	100.12
n	8	8	8	8
$\delta^{18}O_{VPDB}$	-15.6	-15.6	-15.6	-15.6

$\delta^{13}C_{VPDB}$	-47.32	-47.32	-47.32	-47.32
NBS-18 Calcite	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-5.07011	-5.06170	-23.95265	-23.81458
std dev	0.20555	0.20574	0.08786	0.08604
%CV	4.05	4.06	0.37	0.36
%Acc	101.12	100.95	103.24	102.65
n	8	8	8	8
$\delta^{18}O_{VPDB}$	-23.2	-23.2	-23.2	-23.2
$\delta^{13}C_{VPDB}$	-5.014	-5.014	-5.014	-5.014

Table 2:

File name: CO3_060509.XLSX

Standards Statistics $CaCO_3$ and Na_2CO_3 regression				
Secondary	**$\delta^{13}C$**	**$\delta^{18}O$**		
$SrCO_3$	y = 1.0062x - 0.3879	y = 1.0323x - 0.7509		
Leco	y = 1.0062x - 0.393	y = 1.0471x - 0.501		
$CaCO_3$ Merck	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-42.97289	-42.97799	-17.41446	-17.40347
std dev	0.07022	0.07022	0.05108	0.05181
%CV	0.16	0.16	0.29	0.30
%Acc	100.15	100.16	100.19	100.13
n	5	5	5	5
$\delta^{18}O$	-17.38127	-17.38127	-17.38127	-17.38127
$\delta^{13}C$	-42.91009	-42.91009	-42.91009	-42.91009
Na_2CO_3	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-2.03606	-2.04116	-17.86382	-17.85926
std dev	0.15673	0.15673	0.06971	0.07070
%CV	7.70	7.68	0.39	0.40
%Acc	108.68	108.95	99.41	99.38
n	5	5	5	5
$\delta^{18}O$	-17.97011	-17.97011	-17.97011	-17.97011
$\delta^{13}C$	-1.87349	-1.87349	-1.87349	-1.87349
$SrCO_3$	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-4.71954	-4.72464	-13.96379	-13.90332
std dev	0.05806	0.05806	0.10468	0.10618
%CV	1.23	1.23	0.75	0.76
%Acc	99.80	99.91	99.98	99.55
n	7	7	7	7

$\delta^{18}O$	-13.96625	-13.96625	-13.96625	-13.96625
$\delta^{13}C$	-4.7288	-4.7288	-4.7288	-4.7288
Leco	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-15.55377	-15.55887	-21.19602	-21.23924
std dev	0.06495	0.06495	0.08382	0.08502
%CV	0.42	0.42	0.40	0.40
%Acc	99.49	99.52	99.60	99.81
n	5	5	5	5
$\delta^{18}O$	-21.28028	-21.28028	-21.28028	-21.28028
$\delta^{13}C$	-15.6337	-15.6337	-15.6337	-15.6337

File name: CO3_060509.XLSX

Standards				
Statistics				
Primary				
NBS-19	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	1.84547	1.84037	-2.36076	-2.13394
std dev	0.05122	0.05122	0.07319	0.07424
%CV	2.78	2.78	3.10	3.48
%Acc	94.64	94.38	107.31	97.00
n	7	7	7	7
$\delta^{18}O_{VPDB}$	-2.2	-2.2	-2.2	-2.2
$\delta^{13}C_{VPDB}$	1.95	1.95	1.95	1.95
$BaCO_3$	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-47.10668	-47.11178	-15.65833	-15.62216
std dev	0.24446	0.24446	0.07931	0.08044
%CV	0.52	0.52	0.51	0.51
%Acc	99.55	99.56	100.37	100.14
n	8	8	8	8
$\delta^{18}O_{VPDB}$	-15.6	-15.6	-15.6	-15.6
$\delta^{13}C_{VPDB}$	-47.32	-47.32	-47.32	-47.32
NBS-18 Calcite	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-5.11167	-5.11677	-23.72604	-23.80553
std dev	0.06023	0.06023	0.05804	0.05888
%CV	1.18	1.18	0.24	0.25
%Acc	101.95	102.05	102.27	102.61
n	8	8	8	8
$\delta^{18}O_{VPDB}$	-23.2	-23.2	-23.2	-23.2
$\delta^{13}C_{VPDB}$	-5.014	-5.014	-5.014	-5.014

Table 3:

File Name: CO3_061009.xlsx

Standards Statistics $CaCO_3$ and Na_2CO_3 regression		
Secondary	**$\delta^{13}C$**	**$\delta^{18}O$**
$SrCO_3$	y = 1.0061x - 0.427	y = 1.056x - 0.4578
Leco	y = 1.0054x - 0.4737	y = 1.0509x - 0.532

$CaCO_3$ Merck	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-43.01842	-43.03549	-17.48666	-17.47862
std dev	0.10136	0.10129	0.07767	0.07730
%CV	0.24	0.24	0.44	0.44
%Acc	100.25	100.29	100.61	100.56
n	5	5	5	5
$\delta^{18}O$	-17.38127	-17.38127	-17.38127	-17.38127
$\delta^{13}C$	-42.91009	-42.91009	-42.91009	-42.91009

Na_2CO_3	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-1.93214	-1.97779	-17.86608	-17.85620
std dev	0.14363	0.14353	0.06603	0.06572
%CV	7.43	7.26	0.37	0.37
%Acc	103.13	105.57	99.42	99.37
n	5	5	5	5
$\delta^{18}O$	-17.97011	-17.97011	-17.97011	-17.97011
$\delta^{13}C$	-1.87349	-1.87349	-1.87349	-1.87349

$SrCO_3$	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-4.70786	-4.75158	-13.98533	-13.99420
std dev	0.05589	0.05585	0.07832	0.07795
%CV	1.19	1.18	0.56	0.56
%Acc	99.56	100.48	100.14	100.20
n	7	7	7	7
$\delta^{18}O$	-13.96625	-13.96625	-13.96625	-13.96625
$\delta^{13}C$	-4.7288	-4.7288	-4.7288	-4.7288

Leco	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-15.50306	-15.53927	-21.32825	-21.30165
std dev	0.10676	0.10669	0.09096	0.09052
%CV	0.69	0.69	0.43	0.42
%Acc	99.16	99.40	100.23	100.10
n	5	5	5	5
$\delta^{18}O$	-21.28028	-21.28028	-21.28028	-21.28028
$\delta^{13}C$	-15.6337	-15.6337	-15.6337	-15.6337

File Name:
CO3_061009.xlsx

Standards
Statistics
Primary

NBS-19	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	1.87139	1.82309	-2.00466	-2.07139
std dev	0.06229	0.06224	0.07093	0.07059
%CV	3.33	3.41	3.54	3.41
%Acc	95.97	93.49	91.12	94.15
n	7	7	7	7
$\delta^{18}O_{VPDB}$	-2.2	-2.2	-2.2	-2.2
$\delta^{13}C_{VPDB}$	1.95	1.95	1.95	1.95

$BaCO_3$	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-47.23674	-47.25087	-15.63709	-15.63798
std dev	0.14732	0.14722	0.08265	0.08225
%CV	0.31	0.31	0.53	0.53
%Acc	99.82	99.85	100.24	100.24
n	8	8	8	8
$\delta^{18}O_{VPDB}$	-15.6	-15.6	-15.6	-15.6
$\delta^{13}C_{VPDB}$	-47.32	-47.32	-47.32	-47.32

NBS-18 Calcite	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-5.13542	-5.17884	-23.83309	-23.79440
std dev	0.06405	0.06400	0.08618	0.08576
%CV	1.25	1.24	0.36	0.36
%Acc	102.42	103.29	102.73	102.56
n	8	8	8	8
$\delta^{18}O_{VPDB}$	-23.2	-23.2	-23.2	-23.2
$\delta^{13}C_{VPDB}$	-5.014	-5.014	-5.014	-5.014

Table 4:

File Name: Secondary to Primary GB Standards.xlsx

Secondary (Laboratory) Standards - Ave of Three Runs				
$CaCO_3$, Merck	**$\delta^{13}C$ Reg(SrCO3)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-42.98400	-42.99991	-17.46185	-17.45439
std dev	0.10089	0.10376	0.05501	0.05527
%CV	0.23	0.24	0.32	0.32
%Acc	100.17	100.21	100.46	100.42
n	24	24	24	24
$\delta^{18}O_{VPDB}$	-17.38127	-17.38127	-17.38127	-17.38127
$\delta^{13}C_{VPDB}$	-42.91009	-42.91009	-42.91009	-42.91009
Leco-$CaCO_3$	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-15.54381	-15.55790	-21.31081	-21.28807
std dev	0.08302	0.08120	0.11029	0.08122
%CV	0.53	0.52	0.52	0.38
%Acc	99.43	99.52	100.14	100.04
n	24	24	24	24
$\delta^{18}O_{VPDB}$	-21.28028	-21.28028	-21.28028	-21.28028
$\delta^{13}C_{VPDB}$	-15.6337	-15.6337	-15.6337	-15.6337
Na_2CO_3-Fisher	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-1.91534	-1.92850	-17.87215	-17.86338
std dev	0.13878	0.14174	0.04280	0.04305
%CV	7.25	7.35	0.24	0.24
%Acc	102.23	102.94	99.45	99.41
n	24	24	24	24
$\delta^{18}O_{VPDB}$	-17.97011	-17.97011	-17.97011	-17.97011
$\delta^{13}C_{VPDB}$	-1.87349	-1.87349	-1.87349	-1.87349
$SrCO_3$	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-4.68729	-4.70063	-13.96552	-13.97135
std dev	0.08185	0.09289	0.06849	0.08744
%CV	1.75	1.98	0.49	0.63
%Acc	99.12	99.40	99.99	100.04
n	30	30	30	30
$\delta^{18}O_{VPDB}$	-13.96625	-13.96625	-13.96625	-13.96625
$\delta^{13}C_{VPDB}$	-4.7288	-4.7288	-4.7288	-4.7288

File Name: Secondary to Primary GB Standards.xlsx

Primary (International) Standards - Ave of Three Runs				
$BaCO_3$ (IAEA-CO-9)	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-47.24999	-47.26622	-15.62526	-15.62531
std dev	0.20991	0.21612	0.07105	0.06389
%CV	0.44	0.46	0.45	0.41
%Acc	99.85	99.89	100.16	100.16
n	24	24	24	24
$\delta^{18}O_{VPDB}$	-15.6	-15.6	-15.6	-15.6
$\delta^{13}C_{VPDB}$	-47.32	-47.32	-47.32	-47.32
NBS-18 Calcite	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	-5.10533	-5.11870	-23.83704	-23.80462
std dev	0.12628	0.13273	0.11348	0.06314
%CV	2.47	2.59	0.48	0.27
%Acc	101.82	102.09	102.75	102.61
n	24	24	24	24
$\delta^{18}O_{VPDB}$	-23.2	-23.2	-23.2	-23.2
$\delta^{13}C_{VPDB}$	-5.014	-5.014	-5.014	-5.014
NBS-19, $CaCO_3$	**$\delta^{13}C$ Reg($SrCO_3$)**	**$\delta^{13}C$ Reg(Leco)**	**$\delta^{18}O$ Reg($SrCO_3$)**	**$\delta^{18}O$ Reg(Leco)**
ave.	1.90730	1.89441	-2.08404	-2.13713
std dev	0.09766	0.11275	0.21825	0.08985
%CV	5.12	5.95	10.47	4.20
%Acc	97.81	97.15	94.73	97.14
n	21	21	21	21
$\delta^{18}O_{VPDB}$	-2.2	-2.2	-2.2	-2.2
$\delta^{13}C_{VPDB}$	1.95	1.95	1.95	1.95

Table 5:
$\delta^{13}C$ Standard Values Chart (average of three runs)

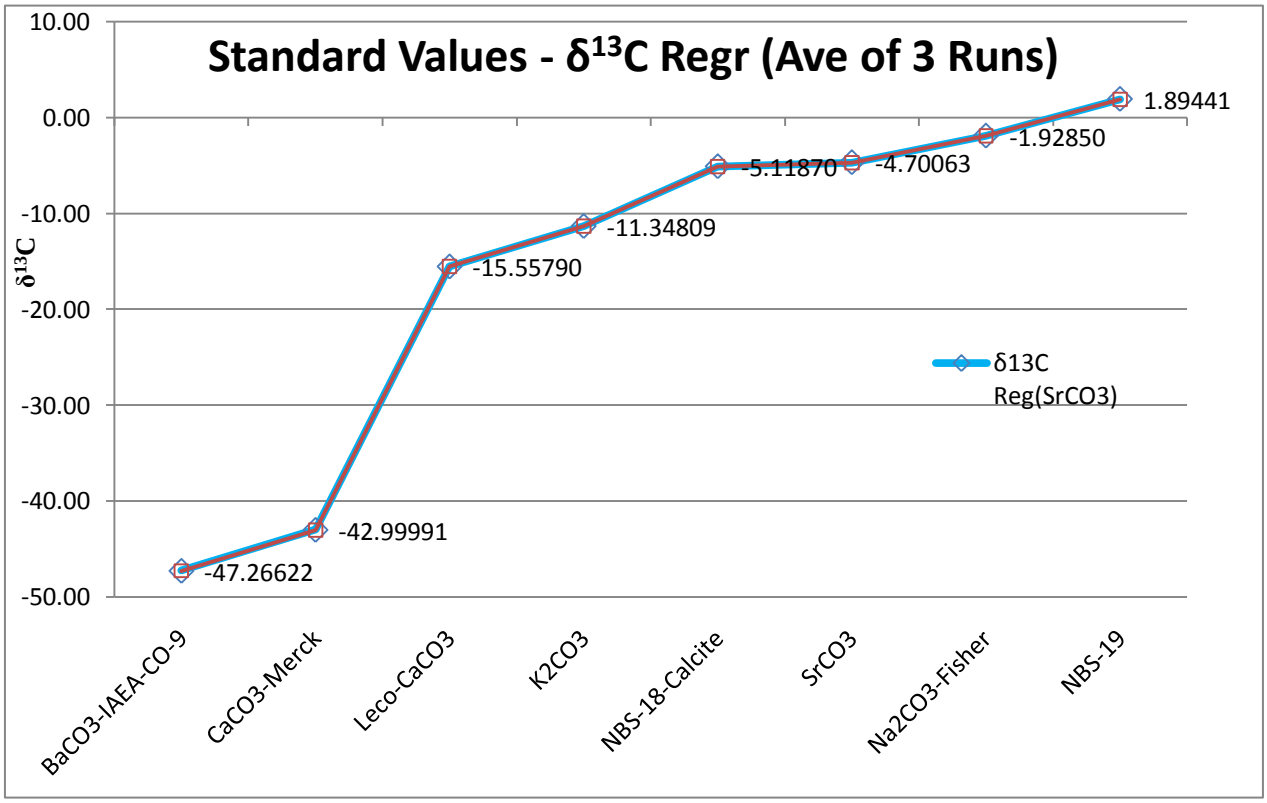

Table 6:
Average of Three Runs (06/01/09, 06/05/09, and 06/10/09) Sorted by $\delta^{13}C$.

Standard	$\delta^{13}C$ Reg($SrCO_3$)	$\delta^{13}C$ Reg(Leco)	$\delta^{18}O$ Reg($SrCO_3$)	$\delta^{18}O$ Reg(Leco)
$BaCO_3$	-47.24999	-47.26622	-15.62526	-15.62531
$CaCO_3$-Merck	-42.98400	-42.99991	-17.46185	-17.45439
Leco-$CaCO_3$	-15.54381	-15.55790	-21.31081	-21.28807
K_2CO_3	-11.33426	-11.34809	-24.04122	-24.00577
NBS-18-Calcite	-5.10533	-5.11870	-23.83704	-23.80462
$SrCO_3$	-4.68729	-4.70063	-13.96552	-13.97135
Na_2CO_3-Fisher	-1.91534	-1.92850	-17.87215	-17.86338
NBS-19	1.90730	1.89441	-2.08404	-2.13713

Table 7:

$\delta^{13}C$ and $\delta^{18}O$ Values, Sorted by $\delta^{18}O$ (average of three runs)

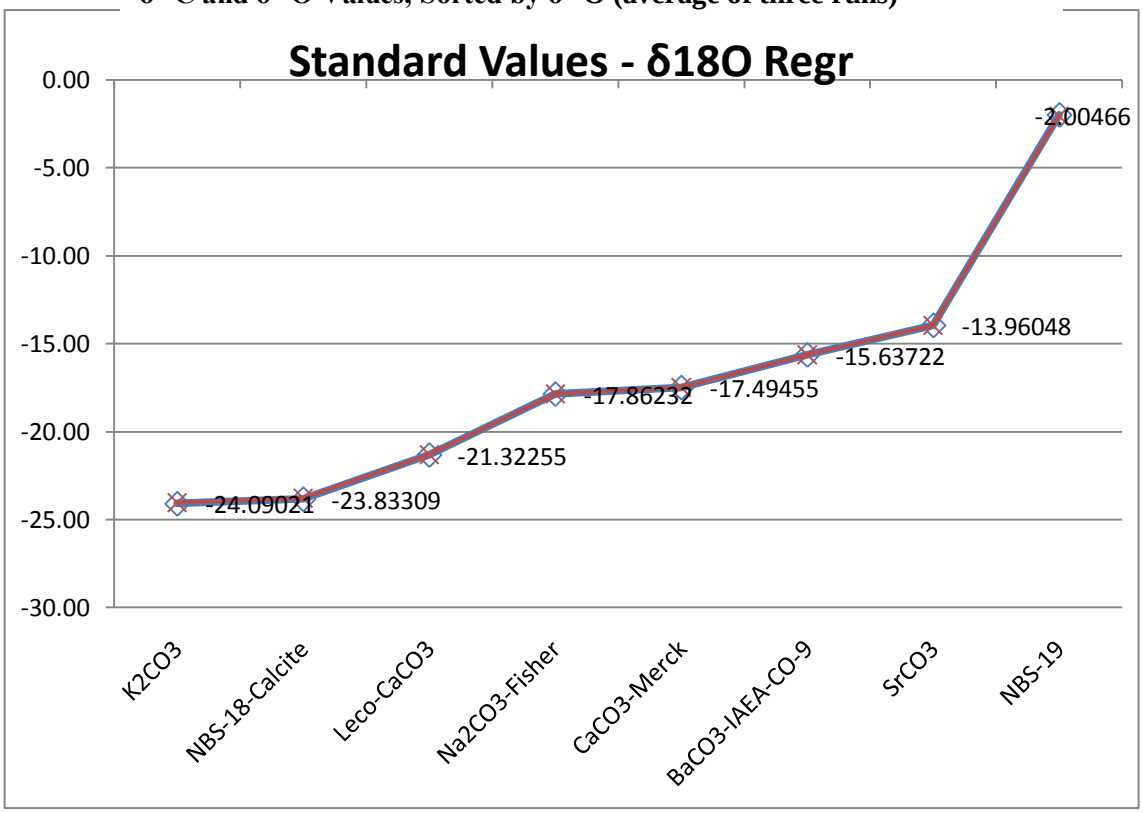

Table 8:

Average of Three Runs (06/01/09, 06/05/09, and 06/10/09)
Sorted by δ18O.

Standard	$\delta^{13}C$ Reg($SrCO_3$)	$\delta^{13}C$ Reg(Leco)	$\delta^{18}O$ Reg($SrCO_3$)	$\delta^{18}O$ Reg(Leco)
K_2CO_3	-11.33426	-11.34809	-24.04122	-24.00577
NBS-18-Calcite	-5.10533	-5.11870	-23.83704	-23.80462
Leco-$CaCO_3$	-15.54381	-15.55790	-21.31081	-21.28807
Na_2CO_3-Fisher	-1.91534	-1.92850	-17.87215	-17.86338
$CaCO_3$-Merck	-42.98400	-42.99991	-17.46185	-17.45439
$BaCO_3$	-47.24999	-47.26622	-15.62526	-15.62531
$SrCO_3$	-4.68729	-4.70063	-13.96552	-13.97135
NBS-19	1.90730	1.89441	-2.08404	-2.13713

Table 9: %Accuracy and %CV

Overall Inter-Statistics					
Secondary , n=102		**$\delta^{13}C$ ($SrCO_3$)**	**$\delta^{13}C$ (Leco)**	**$\delta^{18}O$ ($SrCO_3$)**	**$\delta^{18}O$ (Leco)**
%Acc	Ave=	100.24	100.52	100.01	99.97
%Acc	StDev=	1.40	1.65	0.42	0.42
%CV	Ave=	2.44	2.52	0.39	0.39
%CV	StDev=	3.27	3.31	0.13	0.17
***Primary, n=69**					
%Acc	Ave=	99.83	99.71	99.21	99.97
%Acc	StDev=	2.01	2.47	4.09	2.74
%CV	Ave=	2.68	3.00	3.80	1.63
%CV	StDev=	2.34	2.77	5.78	2.23
Combined, n=171					
%Acc	Ave=	100.06	100.17	99.67	99.97
%Acc	StDev=	1.54	1.90	2.42	1.61
%CV	Ave=	2.54	2.73	1.85	0.92
%CV	StDev=	2.68	2.84	3.80	1.45
*Primary read-back statistics					

3. COMMENTS

It cannot be stressed enough the importance of the proper alignment of the acid dosing needle onto the sample vial cap. Even after a careful check of the alignment during a preliminary CO_3 run, the acid dosing needle broke after ten or twelve samples (apparently by contacting an un-drilled vial cap). The acid entered into the sampling needle and eventually reached the Nafion tubing effectively blocking the gas path. This required the replacement of the Nafion tubing (which was not a simple task!) and the sampling needle.

4. DATA RETRIEVAL

The Raw Data files are stored on the CF-IRMS instrument computer in the GeoSciences laboratory in the following location:

C:\Thermo\Isodat NT\Global\User\Gasbench\Results\CO3_Analysis_Folder\ Filename.xxx. (Note: to view these files you must use Workspace)

The files and data for the carbonate validation are stored on the network in the following location:

Campus on 'ESS'(P:) \Instrumentation\Geosciences\Data\Thermo_IRMS\ GasBench\Carbonate Analysis\filename.xxx.

5. CONCLUSIONS

This analysis determined which carbonate samples would serve as the best potential secondary standards to be used for subsequent carbonate analysis for $\delta^{13}C$ and $\delta^{18}O$. To determine the effect of the diluter on the data, a number of samples were purposely analyzed at two to four times their target weights, this typically activated the diluter. There was no delta value difference noted between sample data acquired with the diluter and data acquired without the diluter. The following is a summary of the results

Secondary Standards for $\delta^{13}C$*:

a. $CaCO_3$-Merck: $\delta^{13}C$ = -42.91009‰, $\delta^{18}O$ = -17.38127‰
b. Na_2CO_3-Fisher: $\delta^{13}C$ = -1.87349‰, $\delta^{18}O$ = -17.97011‰

***Note:** The $\delta^{13}C$ spread (-42.9 1to -1.87) for these two secondary standards is acceptable, the spread for $\delta^{18}O$ (-17.38 to -17.97) is not. Another secondary standard will need to be used to accurately provide $\delta^{18}O$ data.

Potential Secondary Standards for $\delta^{18}O$:

a. $CaCO_3$-Leco: $\delta^{13}C$ = -15.6337‰, $\delta^{18}O$ = -21.28028‰
b. $SrCO_3$-Baker: $\delta^{13}C$ = -4.7288‰, $\delta^{18}O$ = -13.96625‰

Two possible methods for $\delta^{18}O$ analysis are suggested:

1. Use three secondary standards for an analysis: $CaCO_3$-Merck and Na_2CO_3-Fisher for $\delta^{13}C$, and the addition of either $SrCO_3$-Baker or $CaCO_3$-Leco for $\delta^{18}O$, the choice of which secondary standard to use would be made based on the estimate of the $\delta^{18}O$ value of the samples to be analyzed. This is the preferred option.
2. Use $SrCO_3$-Baker in place of Na_2CO_3-Fisher and use two secondary standards for an analysis, this will not give the desired spread for $\delta^{13}C$ as the Na_2CO_3-Fisher, but would provide a better $\delta^{18}O$ spread. This option would allow for more samples to be analyzed per sequence.

6. REFERENCES

Thermo Electron Delta V Advantage Operating Manual

Finnigan GasBench II Operating Manual

7. FIGURES

Figure 1:

PAL Autosampler Methods Used for $\delta^{18}O$ Analysis

Internal No. 1 (A200S-1)*	
Cycle	GC-Inj
Syringe	10 uL
Sample Volume	10.0 uL
Air Volume	0 uL
Pre Cln Slv1	0
Pre Cln Slv2	0
Pre Cln Spl	0
Fill Volume	0 nL
Fill Speed	5.0 uL/s
Fill Strokes	6
Pullup Del	61
Inject to	Flush
Inject Speed	50uL/s
Pre Inj Del	0 ms
Pst Inj Del	0 ms
Pst Cln Slv1	0
Pst Cln Slv2	0

Internal No. 9 (A200S-9)**	
Cycle	GC-Inj
Syringe	10 uL
Sample Volume	10.0 uL
Air Volume	0 uL
Pre Cln Slv1	0
Pre Cln Slv2	0
Pre Cln Spl	0
Fill Volume	0 nL
Fill Speed	5.0 uL/s
Fill Strokes	11
Pullup Del	59 s
Inject to	Flush
Inject Speed	50uL/s
Pre Inj Del	0 ms
Pst Inj Del	0 ms
Pst Cln Slv1	0
Pst Cln Slv2	0

*For FlushFill Sequence

**For Analysis Sequence

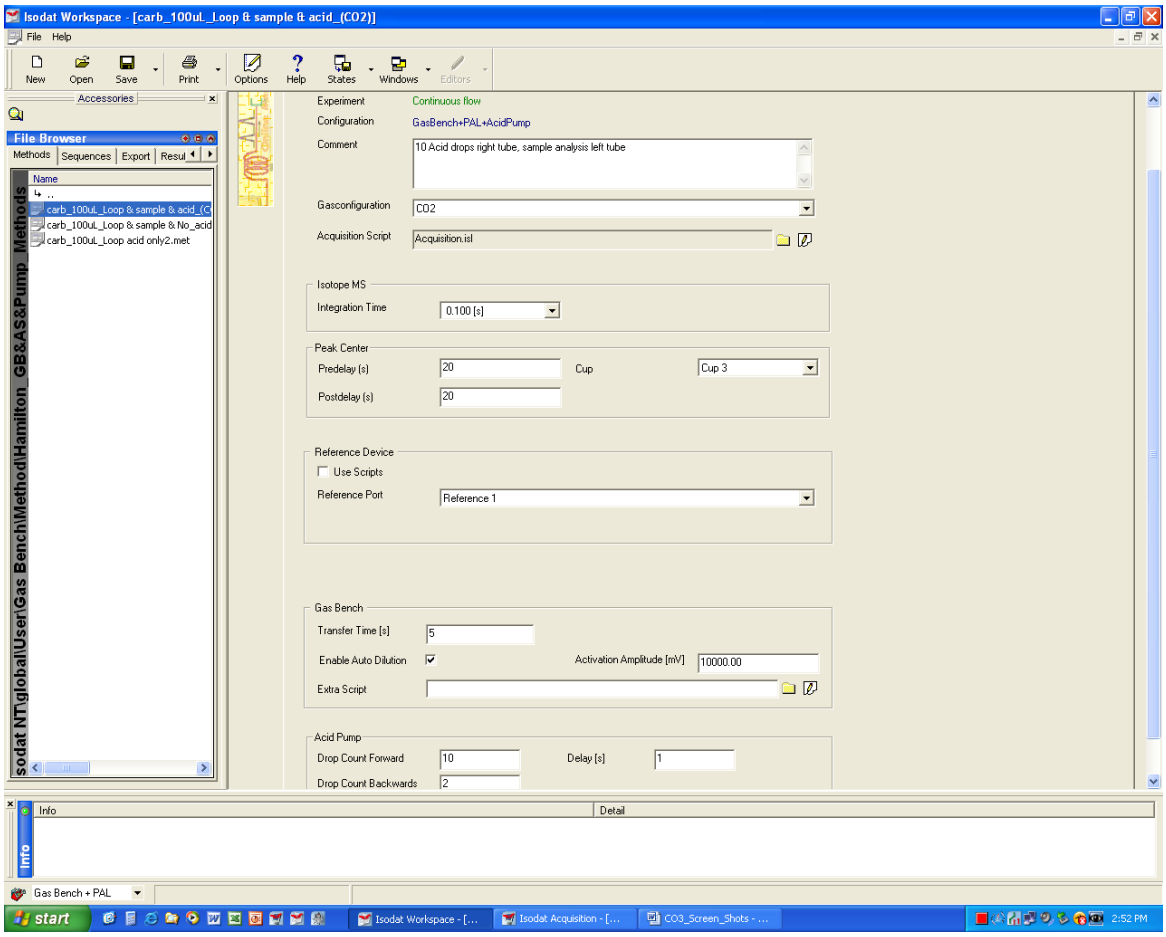

Figure 2: Method File – Instrument Screen

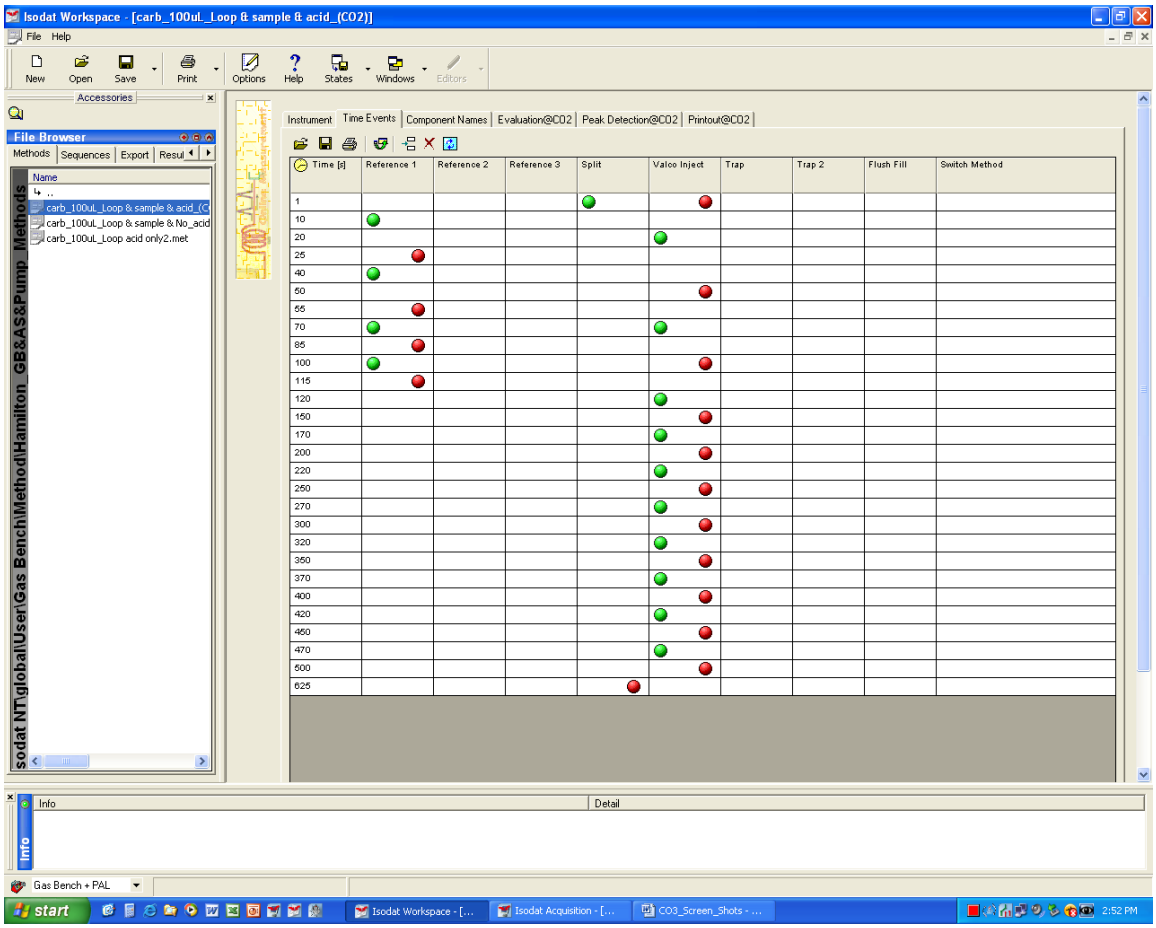

Figure 3: Method File – Time Events Screen

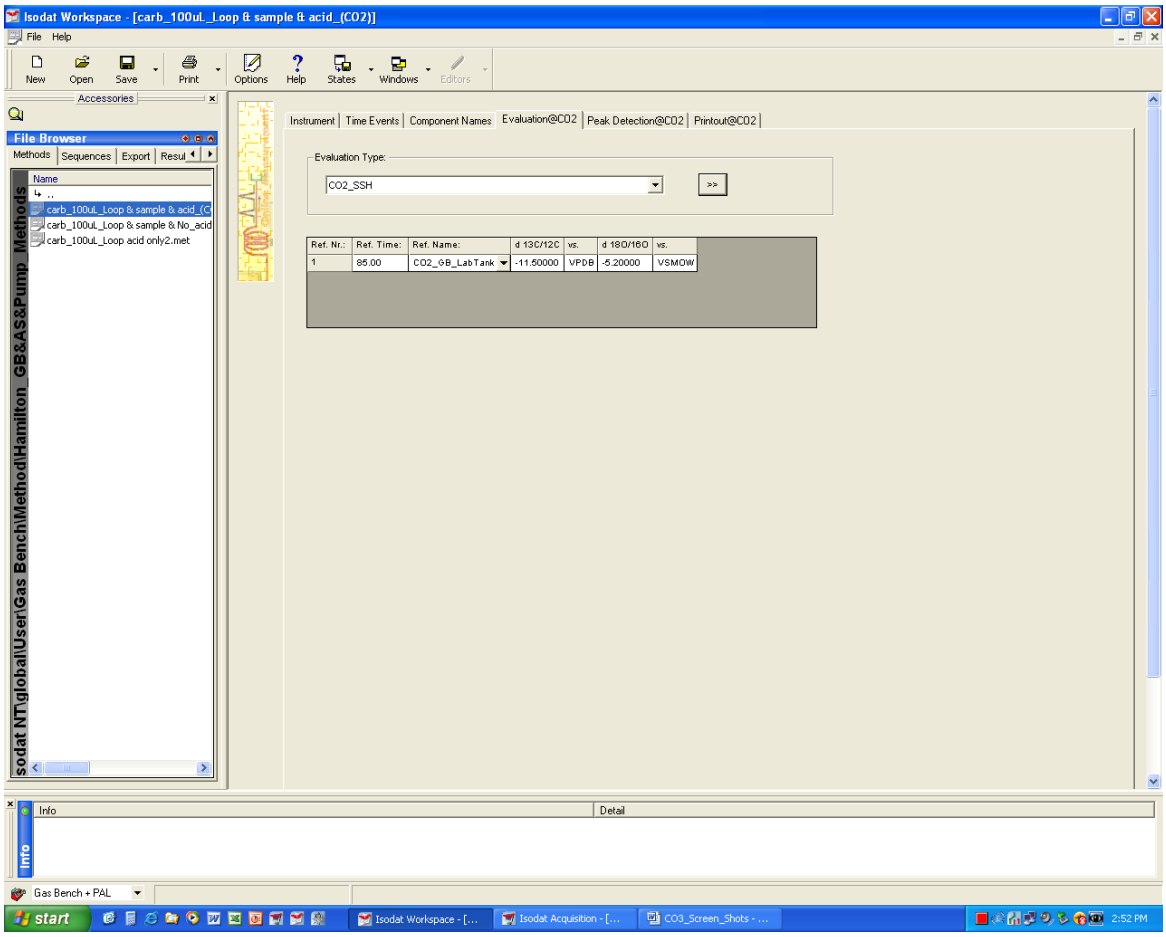

Figure 4: Method File – Evaluation@CO2 Screen

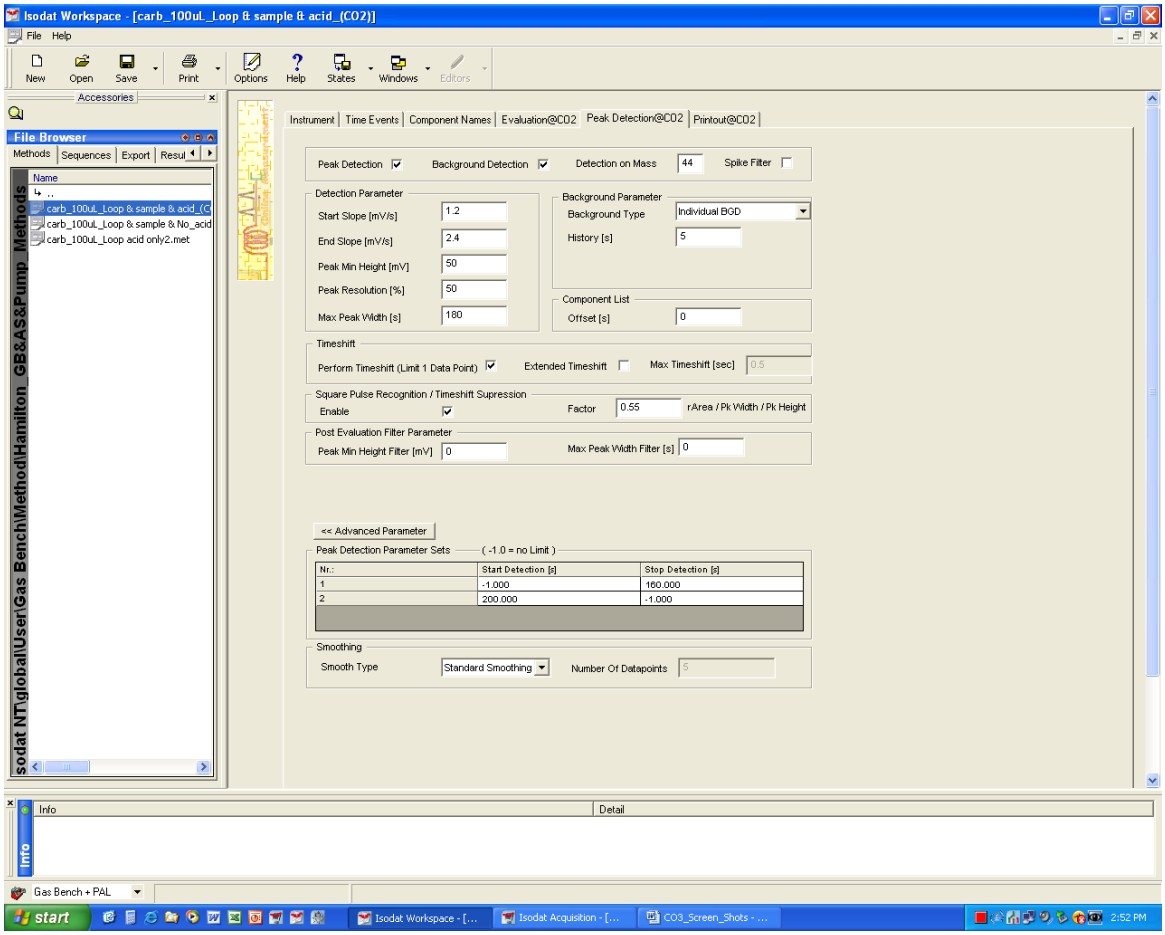

Figure 5: Method File – Peak Detection@CO2 Screen

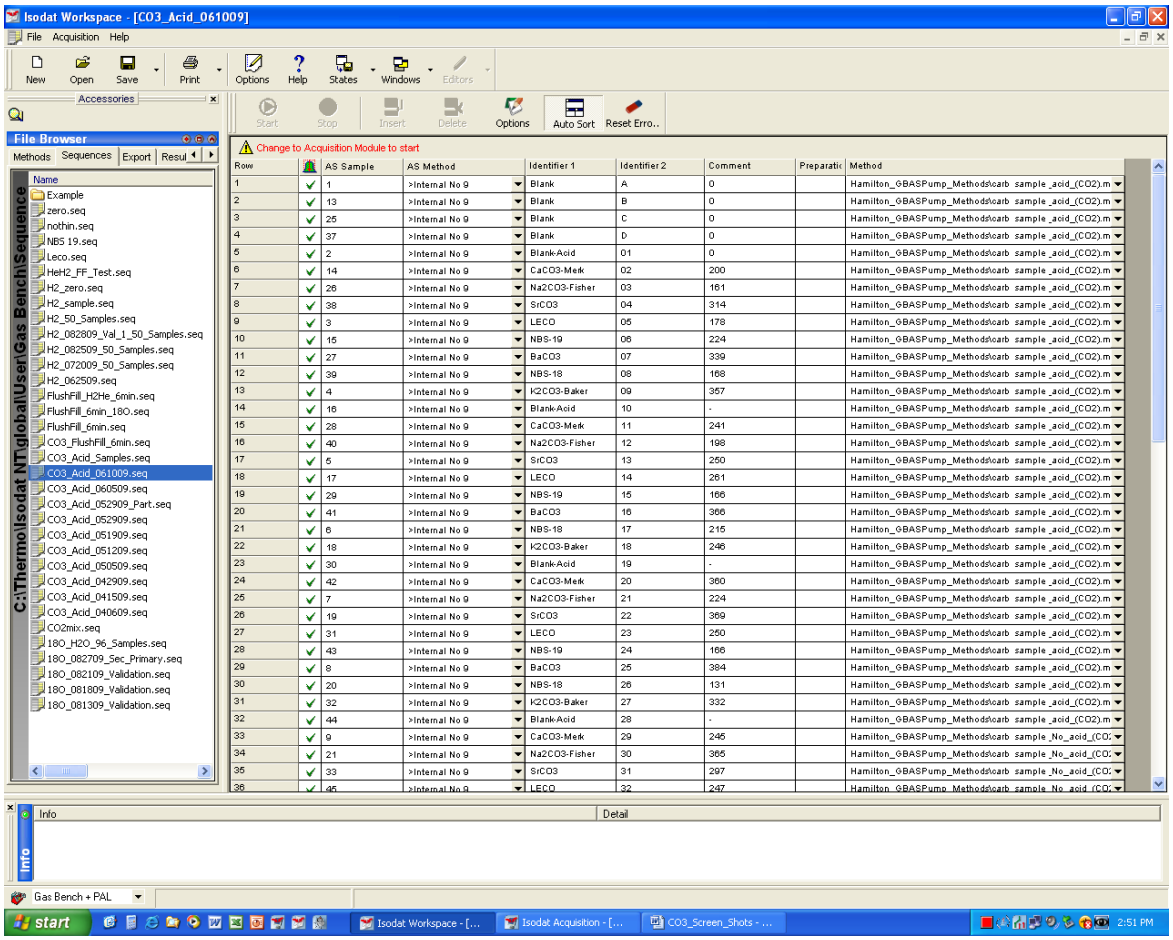

Figure 6: Example of Carbonate Sequence File.

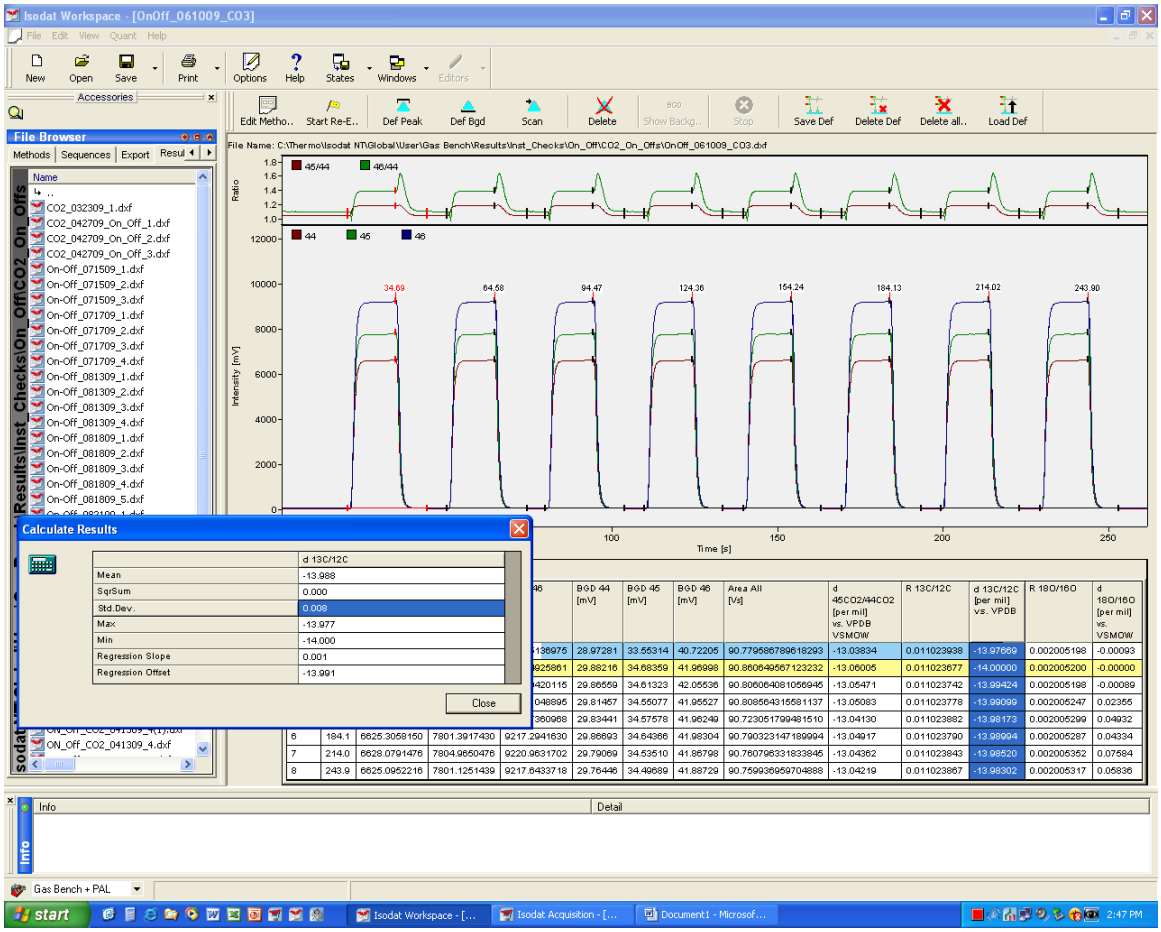

Figure 7: Carbonate On-Off Check (Using CO_2)

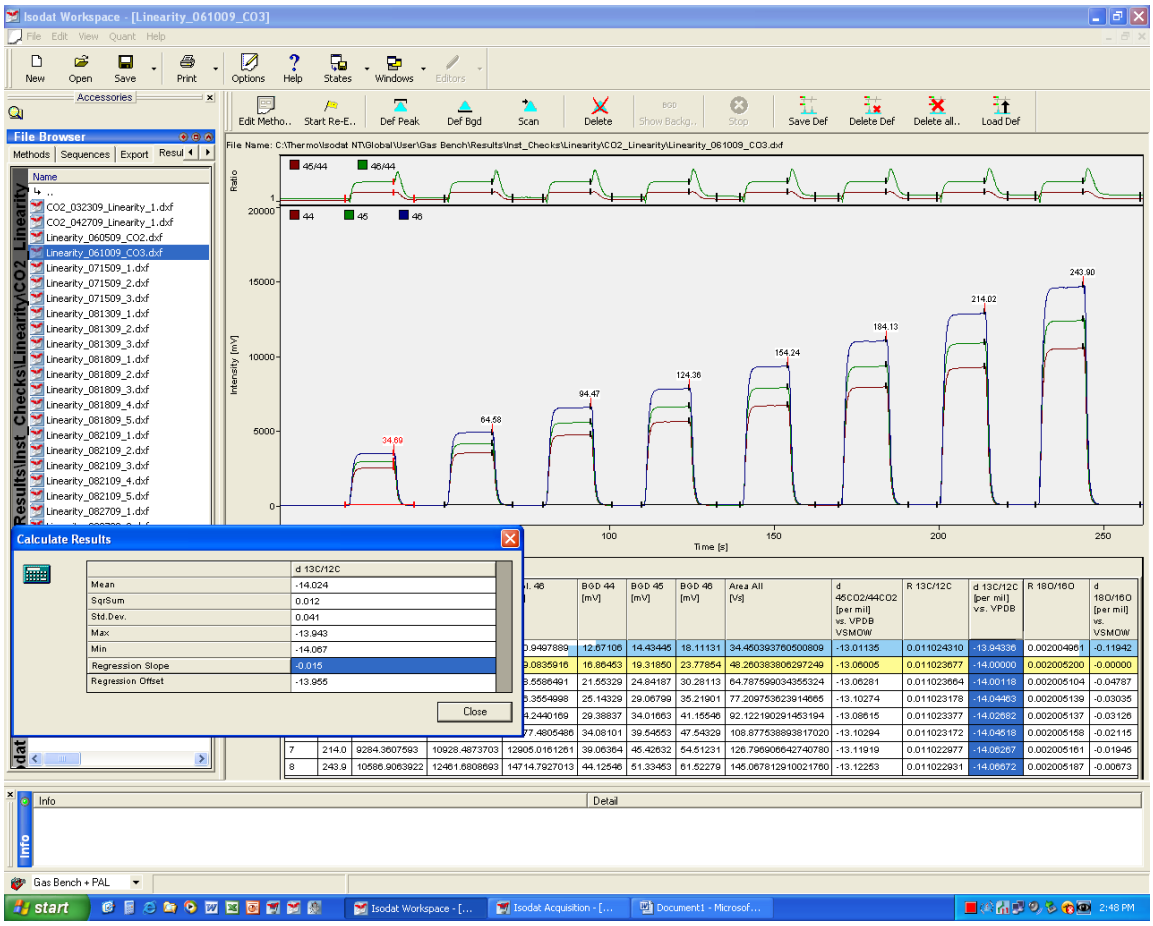

Figure 8: Carbonate Linearity Check (Using CO_2)

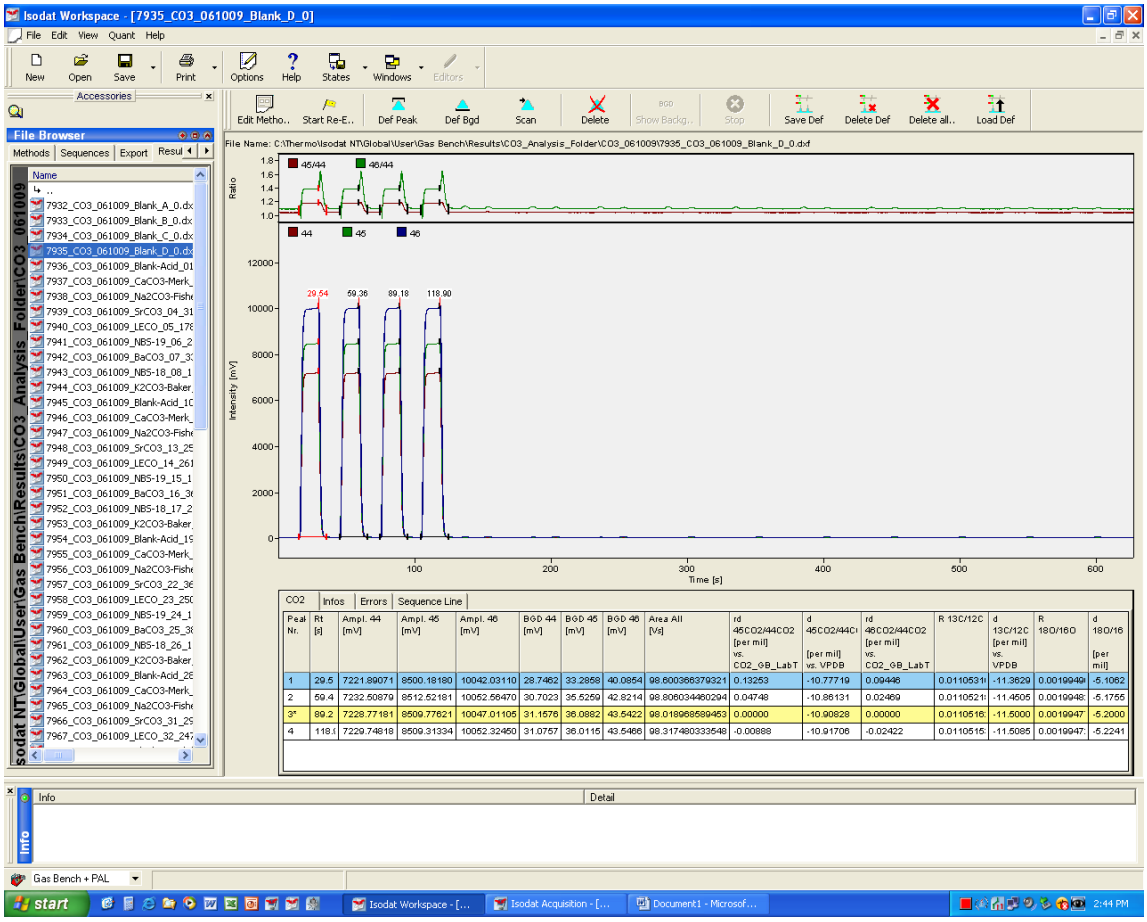

Figure 9: Carbonate Data Acquisition File - Blank

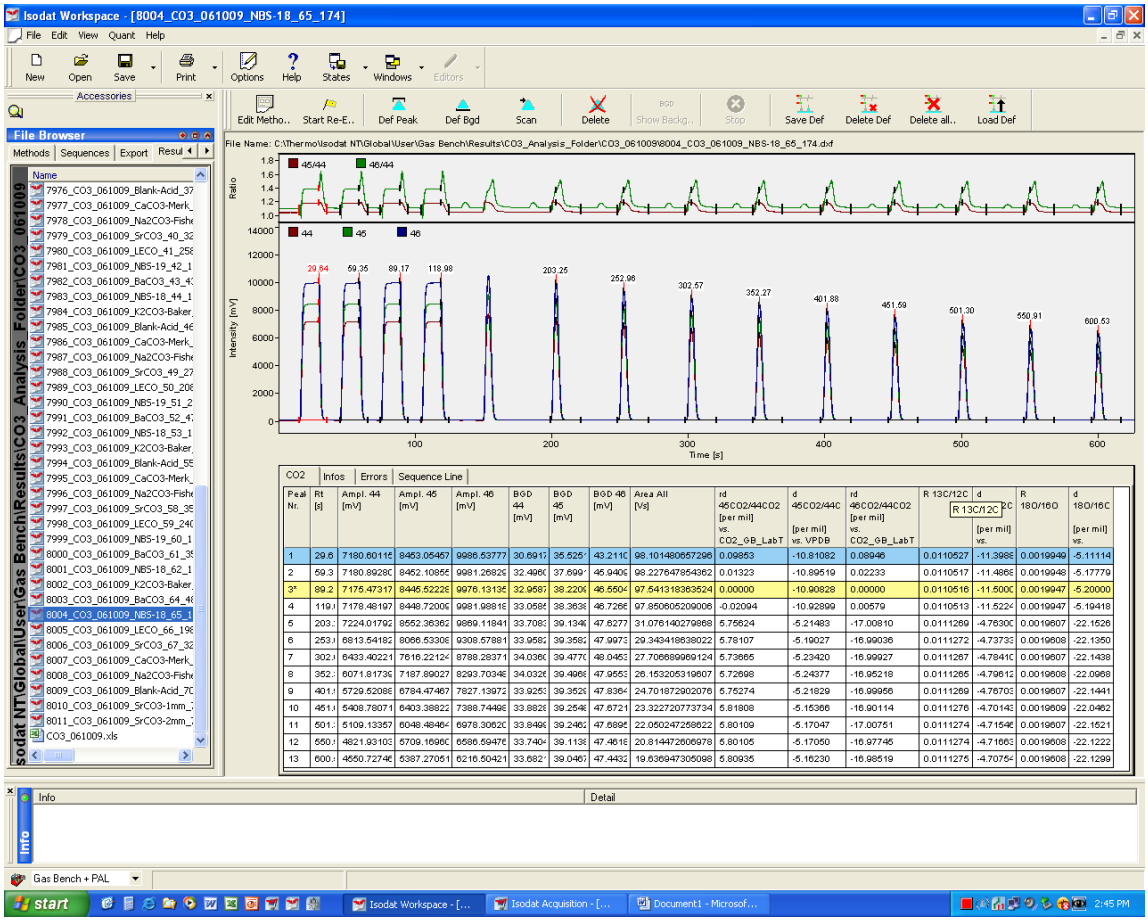

Figure 10: Carbonate Data Acquisition File – Primary Standard (NBS-18)

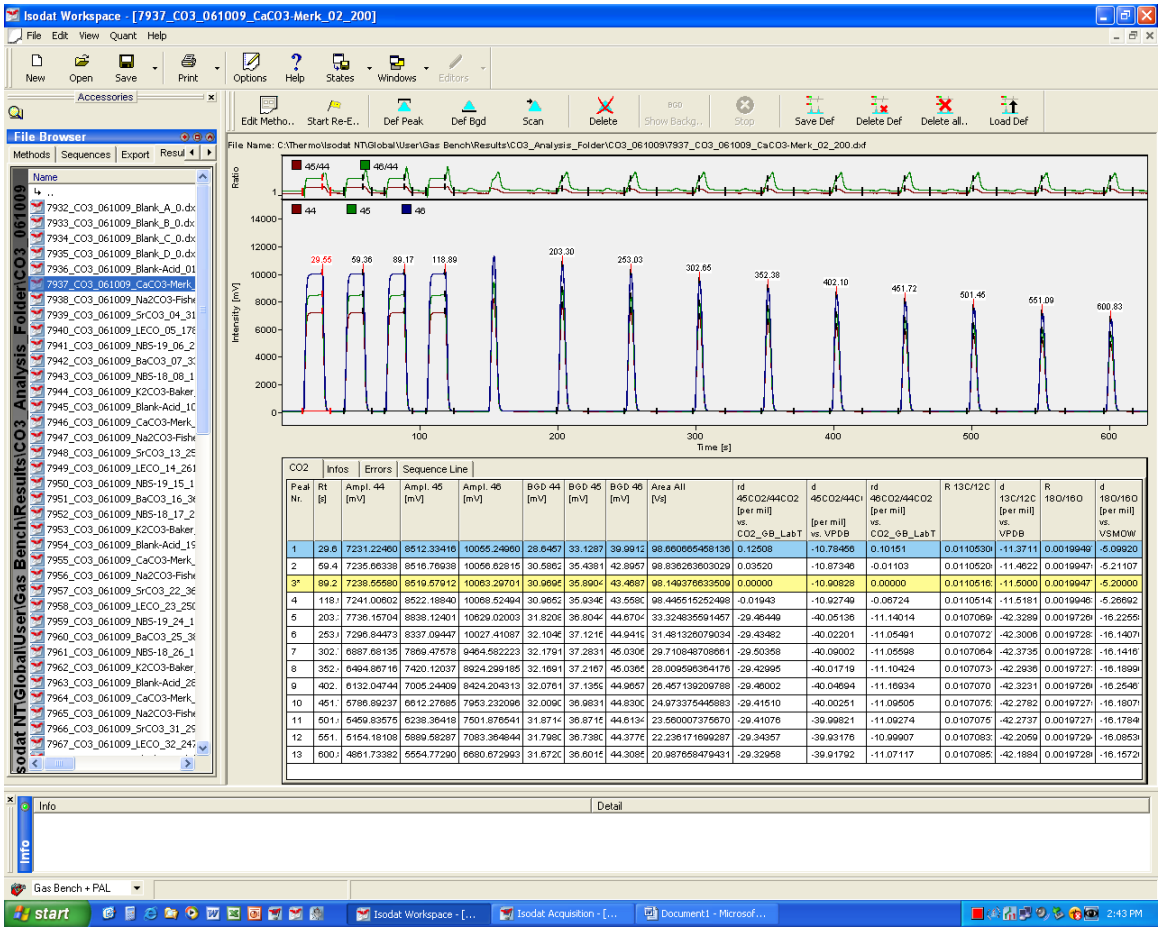

Figure 11: Carbonate Data Acquisition File – Sample ($CaCO_3$ Merck)

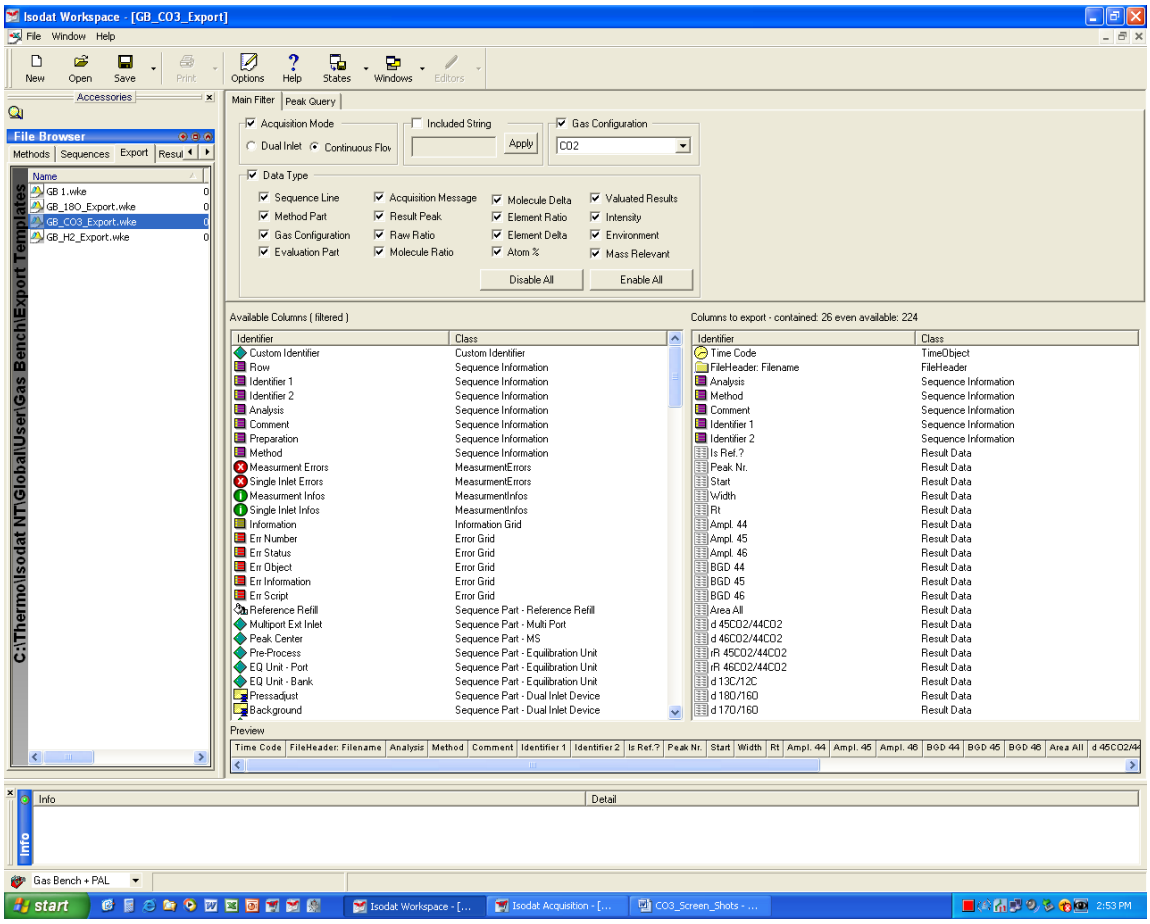

Figure 12: Carbonate Export File – GB_CO3_Export