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 ₂ CO ₃ -Fisher: Lot 946040			
	SrCO ₃ - J.T. Baker: Lot 1424 (7-19b)			
	CaCO ₃ -Leco: Lot No. 1016			
Experimentally Determined	$\frac{\delta^{13}C(SrCO_3)}{\delta^{13}C(Leco)} = \frac{\delta^{13}C(Leco)}{10}$	i		
Values (‰)	CaCO ₃ -Merck: -42.98400 -42.99991 2	4		
	Na ₂ CO ₃ -Fisher: -1.91534 -1.92850 2	4		
	SrCO ₃ - J.T. Baker: -4.68729 -4.70063 3	0		
	CaCO ₃ -Leco: -15.54381 -15.55790 2	4		
	$\frac{\partial^{10}O(SrCO_3)}{\partial^{10}O(Leco)} = \frac{\partial^{10}O(Leco)}{n}$			
	CaCO ₃ -Merck: -17.46185 -17.45439 2	4		
	Na ₂ CO ₃ -Fisher: -17.87215 -17.86338 2	4		
	SrCO ₃ - J.T. Baker: -13.96552 -13.97135 3	0		
	CaCO ₃ -Leco: -21.31081 -21.28807 2	4		
	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: $175 - 275 \mu g$		
	Na ₂ CO ₃ -Fisher: $150 - 250 \mu g$		
	SrCO ₃ - J.T. Baker: $300 - 400 \mu g$		
	CaCO ₃ -Leco: $175 - 275 \mu g$		
Sample Preparation:	Weigh samples and standards.		
r r r	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	Reference Gas: CO ₂ (Ref Gas 1)	
Sample Analysis:	Instrument configuration: GasBench+PAL+Acidpump	
	Fill acid vial in sample block with H ₃ PO 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	δ^{13} C Precision and Accuracy			
Accuracy (Acc)	δ	$5^{13}C(SrCO_3)$	δ^{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 ₂ CO 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	
	s ¹⁸ O D	notician and	A	
	0 01	180(8xCO)	$s^{18}O(L_{000})$	
	BaCO, IAFA-CO-G).	0 O(Leco)	п
	% CV	0.45	0.41	24
	% Acc	100.45	100.41	24
	NBS-18 Calcite	100.10	100.10	
	% CV	0.48	0.27	24
	% Acc	102.75	102.61	2.
	NBS-19, CaCO ₃ :	1021/0	102101	
	% CV	10.47	4.20	21
	% Acc	94.73	97.14	

Inter-assay Precision (CV) and	δ^{18} O Precision and Accuracy (cont.)			
Accuracy (Acc)		$\delta^{18}O(SrCO_3)$	$\delta^{18}O(Leco)$	n
	CaCO ₃ -Merck:			
	% CV	0.32	0.32	24
	% Acc	100.46	100.42	
	Na ₂ CO ₃ -Fisher:			
	% CV	0.24	0.24	24
	% Acc	99.45	99.41	
	SrCO ₃ - J.T. Baker	r:		
	% 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

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1. INTRODUCTION

This report describes the qualification process for carbonate laboratory standards as well as the analysis methods for carbonate analysis of δ^{13} C and δ^{18} O using the automated Gas Bench-Acid Dosing technique. Various carbonates (CaCO₃, K₂CO₃, SrCO₃, and Na₂CO₃) 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 δ^{13} C and δ^{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. SrCO₃ J.T Baker Lot 1424, 7-19b
- 2. Na₂CO₃ Fisher Lot 946040 S263-500
- 3. CaCO₃ Fisher Lot 735383
- 4. K_2CO_3 Baker Lot 806353 Food grade
- 5. $CaCO_3$ Leco Lot No. 1016
- 6. CaCO₃ Merck Lot B649459 544

The three international standards are as follows:

- 1. BaCO₃ 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 acidblanks).

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 CO₃ 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 μ g and 360 μ g.

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 $(73^{\circ}C)$ 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 (H₂O) 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 CO₂, N₂, H₂, 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 δ^{13} C and δ^{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 BaCO₃).
- 2. CO3_051209.xlxs Two primary standards used (NBS-19 and BaCO₃).
- 3. CO3_051909.xlxs Two primary standards used (NBS-19 and BaCO₃).
- 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	δ ¹³ C	δ ¹⁸ Ο	
NBS-19	16	3.85	4.78	
BaCO ₃	16	0.16	0.54	

Average % Accuracy of Known Delta Values				
	n	δ ¹³ C	δ ¹⁸ Ο	
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. CaCO₃-Merck: δ^{13} C = -42.91009‰, δ^{18} O = -17.38127‰
 - b. Na₂CO₃-Fisher: δ^{13} C = -1.87349‰, δ^{18} O = -17.97011‰

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

2.	Po	tential Secondary S	Standards for δ^{18} O:	
	a.	CaCO ₃ -Leco:	δ^{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 δ^{18} O analysis were identified:

- 1. Use three secondary standards for an analysis: CaCO₃-Merck and Na₂CO₃ for δ^{13} C, and the addition of either SrCO₃ or CaCO₃-Leco, the choice of which secondary standard to use would be made based on the estimate of the δ^{18} O value of the samples to be analyzed.
- 2. Use SrCO₃ in place of Na₂CO₃ and use two secondary standards for an analysis, this will not provide as wide a spread for δ^{13} C as the Na₂CO₃, but would give a better δ^{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 CaCO₃-Merck, Na₂CO₃, and SrCO₃ as standards, the second regression used CaCO₃-Merck, Na₂CO₃, and CaCO₃-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 δ^{13} C standards in chart form in order of increasing δ^{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.

File Name: CO3_0	50109.XLSX					
Standards Statistics CaCO ₃ and Na ₂ CO ₃ regression						
Secondary	δ ¹³ C Regression	δ 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				
			δ ¹⁸ Ο	δ ¹⁸ Ο		
CaCO ₃ Merck	δ ¹³ C Reg(SrCO ₃)	δ^{13} C Reg(Leco)	Reg(SrCO ₃)	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		
δ^{18} O	-17.38127	-17.38127	-17.38127	-17.38127		
δ ¹³ C	-42.91009	-42.91009	-42.91009	-42.91009		
			δ ¹⁸ Ο	δ ¹⁸ Ο		
Na ₂ CO ₃	δ^{13} C Reg(SrCO ₃)	δ ¹³ C Reg(Leco)	Reg(SrCO ₃)	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		
δ ¹⁸ Ο	-17 97011	-17 97011	-17 97011	-17 97011		

Table 1:

δ ¹³ C	-1.87349	-1.87349	-1.87349	-1.87349
			δ ¹⁸ Ο	δ ¹⁸ Ο
SrCO ₃	δ ¹³ C Reg(SrCO ₃)	δ ¹³ C Reg(Leco)	Reg(SrCO ₃)	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
δ ¹⁸ Ο	-13.96625	-13.96625	-13.96625	-13.96625
δ ¹³ C	-4.7288	-4.7288	-4.7288	-4.7288
			δ^{18} O	δ ¹⁸ Ο
Leco	δ ¹³ C Reg(SrCO ₃)	δ ¹³ C Reg(Leco)	Reg(SrCO ₃)	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
δ ¹⁸ Ο	-21.28028	-21.28028	-21.28028	-21.28028
δ ¹³ C	-15.6337	-15.6337	-15.6337	-15.6337

File Name:

CO3 0	60109.X	LSX
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Standards				
Statistics				
Primary				
NDC 10		slap ($\delta^{18}O$	$\delta^{18}O$
<u>NBS-19</u>	$\delta^{13}C \operatorname{Reg}(\operatorname{SrCO}_3)$	δ ¹⁵ C Reg(Leco)	$\operatorname{Reg}(\operatorname{SrCO}_3)$	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
			δ ¹⁸ Ο	δ ¹⁸ O
BaCO ₃	δ^{13} C Reg(SrCO ₃)	δ ¹³ C Reg(Leco)	Reg(SrCO ₃)	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
			δ ¹⁸ Ο	δ ¹⁸ Ο
NBS-18 Calcite	δ^{13} C Reg(SrCO ₃)	δ^{13} C Reg(Leco)	Reg(SrCO ₃)	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 ₂ CO ₃ regression				
Secondary	δ ¹³ C	δ ¹⁸ Ο		
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	δ ¹³ C Reg(SrCO ₃)	δ ¹³ C Reg(Leco)	δ ¹⁸ O Reg(SrCO ₃)	δ 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
δ ¹⁸ Ο	-17.38127	-17.38127	-17.38127	-17.38127
δ ¹³ C	-42.91009	-42.91009	-42.91009	-42.91009
Na ₂ CO ₃	δ ¹³ C Reg(SrCO ₃)	δ ¹³ C Reg(Leco)	δ ¹⁸ O Reg(SrCO ₃)	δ 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
δ ¹⁸ Ο	-17.97011	-17.97011	-17.97011	-17.97011
δ ¹³ C	-1.87349	-1.87349	-1.87349	-1.87349
SrCO ₃	δ^{13} C Reg(SrCO ₃)	δ ¹³ C Reg(Leco)	δ ¹⁸ O Reg(SrCO ₃)	δ 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
δ ¹³ C	-4.7288	-4.7288	-4.7288	-4.7288
Leco	δ^{13} C Reg(SrCO ₃)	δ^{13} C Reg(Leco)	δ^{18} O Reg(SrCO ₃)	δ 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
δ ¹⁸ Ο	-21.28028	-21.28028	-21.28028	-21.28028
δ ¹³ C	-15.6337	-15.6337	-15.6337	-15.6337

File name:	CO3_	_060509	.XLSX
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Standards				
Statistics				
Primary				
NBS-19	δ^{13} C Reg(SrCO ₃)	δ ¹³ C Reg(Leco)	δ ¹⁸ O Reg(SrCO ₃)	δ 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	δ ¹³ C Reg(SrCO ₃)	δ ¹³ C Reg(Leco)	δ ¹⁸ O Reg(SrCO ₃)	δ 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	δ^{13} C Reg(SrCO ₃)	δ ¹³ C Reg(Leco)	δ ¹⁸ O Reg(SrCO ₃)	δ 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	Standards Statistics CaCO ₃ and Na ₂ CO ₃ regression						
Secondary	δ ¹³ C	δ^{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					
	-	-					
			δ ¹⁸ Ο	δ ¹⁸ Ο			
CaCO ₃ Merck	δ^{13} C Reg(SrCO ₃)	δ^{13} C Reg(Leco)	Reg(SrCO₃)	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			
δ ¹⁸ Ο	-17.38127	-17.38127	-17.38127	-17.38127			
$\delta^{13}C$	-42.91009	-42.91009	-42.91009	-42.91009			
ů č	, 100,	, 100,	,1000	,100,			
			δ ¹⁸ Ο	δ ¹⁸ Ο			
NacCo	δ ¹³ C Reg(SrCO ₂)	δ^{13} C Reg(Leco)	Reg(SrCO ₂)	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			
	103.13	105 57	99.42	99.37			
n	5	5	5	5			
δ ¹⁸ Ο	-17 97011	-17 97011	-17 97011	-17 97011			
δ ¹³ C	-1 87349	-1 87349	-1 87349	-1 87349			
0 C	1.07547	1.07547	1.07547	1.07549			
			δ ¹⁸ Ω	δ ¹⁸ Ο			
SrCO.	δ ¹³ C Reg(SrCO ₂)	δ^{13} C Reg(Leco)	Reg(SrCO.)				
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			
	99.56	100.48	100.14	100.20			
n	7	7	7	7			
δ ¹⁸ Ο	-13 96625	-13 96625	-13 96625	-13 96625			
δ ¹³ C	-4 7288	-4 7288	-4 7288	-4 7288			
0 C	4.7200	4.7200	4.7200	4.7200			
			δ ¹⁸ Ω	δ ¹⁸ Ω			
Laco	δ^{13} C Reg(SrCO.)	δ^{13} C Reg(Leco)	Beg(SrCO.)				
	15 50306	15 53027	21 32825	21 30165			
ave. std dov	-13.30300	0 10669	0.00006	-21.30103			
	0.10070	0.10009	0.09090	0.09052			
	0.07	0.05	100.43	100.42			
/oAtt	57.10 5	57.40 5	5	5			
и \$ ¹⁸ 0	21 20020	J 21 20020	21 20020	5 21 20020			
о О s ¹³ С	-21.20020	-21.20020	-21.20020	-21.20020			
0 U	-13.0337	-13.0337	-13.0337	-13.0337			

File Name:

CO3_061009.xlsx				
Standards				
Statistics				
Primary				
			δ ¹⁸ Ο	δ ¹⁸ Ο
<u>NBS-19</u>	δ^{13} C Reg(SrCO ₃)	δ^{13} C Reg(Leco)	Reg(SrCO ₃)	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
			δ ¹⁸ Ο	δ^{18} O
BaCO ₃	δ^{13} C Reg(SrCO ₃)	δ ¹³ C Reg(Leco)	Reg(SrCO ₃)	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
			δ ¹⁸ Ο	δ ¹⁸ Ο
NBS-18 Calcite	δ ¹³ C Reg(SrCO ₃)	δ ¹³ C Reg(Leco)	Reg(SrCO ₃)	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	δ ¹³ C Reg(SrCO3)	δ ¹³ C Reg(Leco)	δ ¹⁸ O Reg(SrCO ₃)	δ 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	δ ¹³ C Reg(SrCO ₃)	δ ¹³ C Reg(Leco)	δ ¹⁸ O Reg(SrCO ₃)	δ 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 ₂ CO ₃ -Fisher	δ ¹³ C Reg(SrCO ₃)	δ ¹³ C Reg(Leco)	δ ¹⁸ O Reg(SrCO ₃)	δ 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	δ ¹³ C Reg(SrCO ₃)	δ ¹³ C Reg(Leco)	δ ¹⁸ O Reg(SrCO ₃)	δ 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	
$\delta^{13}C_{\text{VPDB}}$	-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	δ ¹³ C Reg(SrCO ₃)	δ ¹³ C Reg(Leco)	δ ¹⁸ O Reg(SrCO ₃)	δ ¹⁸ O Reg(Leco)		
(IAEA-CO-9)						
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	δ ¹³ C Reg(SrCO ₃)	δ ¹³ C Reg(Leco)	δ ¹⁸ O Reg(SrCO ₃)	δ 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	δ ¹³ C Reg(SrCO ₃)	δ ¹³ C Reg(Leco)	δ ¹⁸ O Reg(SrCO ₃)	δ 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 δ^{13} C.

	δ ¹³ C			δ ¹⁸ Ο
Standard	Reg(SrCO ₃)	δ ¹³ C Reg(Leco)	δ ¹⁸ O Reg(SrCO ₃)	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 ₂ CO 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 ₂ CO ₃ -Fisher	-1.91534	-1.92850	-17.87215	-17.86338
NBS-19	1.90730	1.89441	-2.08404	-2.13713



Table 8:

Average of Three Runs (06/01/09, 06/05/09, and 06/10/09) Sorted by δ 18O.

			$\delta^{18}O$	$\delta^{18}O$
Standard	δ^{13} C Reg(SrCO ₃)	δ^{13} C Reg(Leco)	$Reg(SrCO_3)$	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 ₂ CO 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

Overall Inter-Statistics						
Secondary , n=102		$\delta^{13}C$ (SrCO ₃)	$\delta^{13}C$ (Leco)	$\delta^{18}O(SrCO_3)$	δ^{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						

Table 9: %Accuracy and %CV

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 δ^{13} C and δ^{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:	δ^{13} C = -42.91009‰,	δ^{18} O = -17.38127‰
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b. Na₂CO₃-Fisher: δ^{13} C = -1.87349‰, δ^{18} O = -17.97011‰

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

Potential Secondary Standards for δ^{18} O:

a.	CaCO ₃ -Leco:	δ^{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 δ^{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 SrCO₃-Baker or CaCO₃-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 SrCO₃-Baker in place of Na₂CO₃-Fisher and use two secondary standards for an analysis, this will not give the desired spread for δ^{13} C as the Na₂CO₃-Fisher, but would provide a better δ^{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 δ^{18} O Analysis

Internal No. 1 (A200S-1)*		Internal No. 9 (A200S-	9)**		
Cycle	GC-Inj	Cycle	GC-Inj		
Syringe	10 uL	Syringe	10 uL		
Sample Volume	10.0 uL	Sample Volume	10.0 uL		
Air Volume	0 uL	Air Volume	0 uL		
Pre Cln Slv1	0	Pre Cln Slv1	0		
Pre Cln Slv2	0	Pre Cln Slv2	0		
Pre Cln Spl	0	Pre Cln Spl	0		
Fill Volume	0 nL	Fill Volume	0 nL		
Fill Speed	5.0 uL/s	Fill Speed	5.0 uL/s		
Fill Strokes	6	Fill Strokes	11		
Pullup Del	61	Pullup Del	59 s		
Inject to	Flush	Inject to	Flush		
Inject Speed	50uL/s	Inject Speed	50uL/s		
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*For FlushFill Sequence

**For Analysis Sequence

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Figure 2: Method File – Instrument Screen

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Figure 3: Method File – Time Events Screen

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Figure 4: Method File – Evaluation@CO2 Screen

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Figure 5: Method File – Peak Detection@CO2 Screen

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Figure 6: Example of Carbonate Sequence File.



Figure 7: Carbonate On-Off Check (Using CO₂)

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Figure 8: Carbonate Linearity Check (Using CO₂)



Figure 9: Carbonate Data Acquisition File - Blank

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8000_CO3_061009_BaC03_61_3		1 25	9.6 7180.60116	8453.05457	9986.53777	30.6917	35.525'	43.2110	98.101480657296	0.09853	-10.81082	0.08946	0.0110527	-11.398E	0.0019949	-5.11114
8002 CO3 061009 K2CO3-Baker		2 5%	0.3 7180.89280	8462.10855	9981.26825	32.4960	37.6991	45.9405	98.22/64/864362	0.01323	-10.89519	0.02233	0.0110517	-11.4808	0.0019948	-5.1/7/9
2 3003_CO3_061009_BaCO3_64_4		0	0 1 7479 49407	9449 72000	0004.00045	32.9007	20 2826	40.5504	97.541318303524	0.00000	10.00020	0.00000	0.0110510	-11.500C	0.0019947	5.20000
💆 🎽 8004_CO3_061009_NB5-18_65_1		5 20	18.7 7 17 0.40 187 12 : 7224 04705	0560 26265	0980 119/11	22 7095	20.12/0	47.6277	21.0761/0270969	5 75824	5 24/02	17.00910	0.01110010	4 76200	0.0010807	22.1628
2 8005_CO3_061009_LECO_66_19		6 24	31 6813.54192	8066.53309	9308.57881	33,9581	39.3581	47.9975	29.343418638022	5.78107	-5.19027	-16,99036	0.0111272	4.737%	0.0019608	-22.1350
8006_CO3_061009_SrCO3_67_32		7 30	2.1 6433.40221	7616.22124	8788,28371	34.0360	39.4770	48.0453	27.706689969124	5.73665	-5.23420	-16.99927	0.0111287	-4.78410	0.0019607	-22.1438
800/_C03_061009_CaC03-Merk_		8 34	52. 6071.81739	7187.89027	8293.70346	34.0326	39,4965	47.9553	26.153205319807	5.72698	-5.24377	-16.95218	0.0111265	-4.79612	0.0019608	-22.0968
9 8009_CO3_061009_Blank-Acid 70		9 4	11 6729.52088	6784.47467	7827.13972	33.9253	39.3526	47.8364	24.701872902076	5.75274	-5.21829	-16.99956	0.0111269	-4.76703	0.0019807	-22.1441
5rCO3-1mm_		10 46	51.1 5408.78071	6403.38822	7388.74496	33.8828	39.254	47.8721	23.322720773734	5.81808	-5.15366	-16.90114	0.0111276	-4.70143	0.0019609	-22.0462
T 28011_CO3_061009_SrCO3-2mm_:		11 50	01: 6109.13367	6048.48464	6978.3062C	33.8496	39.2462	47.6895	22.050247258622	5.80109	-5.17047	-17.00751	0.0111274	-4.71546	0.0019607	-22.1521
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Figure 10: Carbonate Data Acquisition File – Primary Standard (NBS-18)

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🕊 💆 7952_CO3_061009_NB5-18_17_2										[per mil]	feer mill	[per mil]		[per mil]		[permil]
5 2 7953_CO3_061009_K2CO3-Baker										CO2_GB_LabT	vs. VPDB	CO2_GB_LabT		VPDB		VSMOW
5 7954_CO3_061009_Blank-Acid_15		1 2	29.6 7231.2	2460 8512.3341	10055.24960	28.6457	33.1287	39.9912	98.660665458136	0.12508	-10.78456	0.10151	0.0110530	-11.3711 0.	0019949	-5.09920
27955_CO3_061009_CaCO3-Merk_		2 8	59.4 7235.6	338 8516.7693	10056.62815	30.5862	35.4381	42.8957	98.836263603029	0.03520	-10.87346	-0.01103	0.0110520	-11.4622 0.	0019947:	-5.21107
7957 CO3 061009 5rCO3 22 36		3* 8	39.2 7238.5	5580 8519.5791	2 10063.29701	30.9695	35.8904	43.4687	98.149376633509	0.00000	-10.90828	0.00000	0.0110516:	-11.5000 0.	0019947	-5.20000
9 7958_CO3_061009_LEC0_23_250		4 '	118./ 7241.0	602 8522.1884	10068.52494	30.9652	35.9346	43.5580	98.445515252498	-0.01943	-10.92749	-0.06724	0.0110514	-11.5181 0.	0019946:	-5.26692
9 27959_CO3_061009_NB5-19_24_1		5 2	203: 7736.1	5704 8838.1240	1 10629.02003	31.8205	36.8044	44.6704	33.324835591457	-29.46449	-40.05136	-11.14014	0.0107069:	-42.3289 0.	0019726	-16.2255
7960_CO3_061009_BaCO3_25_3		6 2	253.1 7296.8	473 8337.0944	10027.41087	32.1046	37.1216	44.9419	31.481326079034	-29.43482	-40.02201	-11.05491	0.0107072	-42.3006 0.	0019728	-16.1407
7961_CO3_061009_NB5-18_26_1			302. 6887.6	735 7859.4757	9464.582223	32.1791	37.2831	46.0306	29.710848708661	-29.50358	-40.09002	-11.05598	0.0107064	-42.3735 0.	0019728	-10.1415
7963 CO3 061009 Blank-Arid 25			102 8494.8	710 7420.1203	0924.299185	32.1091	37.2167	40.0365	20.009090304170	-29.42995	-40.04601	11.10424	0.010/073	-42.2930 0.	0019727:	10.1899
9 7964_CO3_061009_CaCO3-Merk		10	151 5799 0	2227 BB12 2780	7053 232006	32.0761	36.0924	44.9057	20.40/139209/88	-28.40002	-40.00254	-11.10934	0.0107070	.42 2792 0	0019720	-10.2040
7965_CO3_061009_Na2CO3-Fishe		11	501: 5459.9	575 6238 3644	7501.876544	31.8744	36 8714	44.6124	23 560007375670	-29.41076	-39.99824	.11.08000	0.0107075	.42 2737 0	0019727	16 1784
2 7966_CO3_061009_5rCO3_31_25		12 8	551 5154.1	3108 5889 5828	7 7083 384844	31 7980	36 7380	44.3776	22 238171699287	.29.34357	-39.93176	-10.99907	0.0107083	-42 2059 01	0010727	18 0853
9 2967_CO3_061009_LECO_32_247		13 6	300: 4861.7	382 5554,7729	6680.672993	31.6720	36.6015	44,3085	20.987658479431	-29.32958	-39.91792	-11.07117	0.0107085	-42.1884 0	0019728	-16.1572
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Figure 11: Carbonate Data Acquisition File – Sample (CaCO₃ Merck)

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Figure 12: Carbonate Export File – GB_CO3_Export