Data reduction for water equilibrations

ASU-W. M. Keck Laboratory for Environmental Geochemistry

Standards:

A minimum of 6 runs of three different standards should be run. Standards are chosen so that two of them bracket the sample data and the third one falls in between as a linearity check.

Processing Results:

All data should be exported to excel. No sorting or trimming should be done on the raw data. Rather, copy the results into a second worksheet and start sorting from there. Here is the appropriate sorting sequence:

Processing Results:

All data should be exported to excel. No sorting or trimming should be done on the raw data. Rather, copy the results into a second worksheet and start sorting from there. Here is the appropriate sorting sequence:

1) Open the export spreadsheet with the raw data from your sequence

Line	Identifier 1	Identifier 2	Analysis	Gasconfigu	Time	Time Code	Is Ref _	Rt	Area All	Ampl 44	d 18O/16O
1	DMSW_standard	18-O_-23.23	2325	CO2	16:47:46	2005/08/23	1	34.9	80.4097	4064	0
1	DMSW_standard	18-O_-23.23	2325	CO2	16:47:46	2005/08/23	1	84.8	80.659	4068	0
1	DMSW_standard	18-O_-23.23	2325	CO2	16:47:46	2005/08/23	1	134.5	80.1692	4040	0
1	DMSW_standard	18-O_-23.23	2325	CO2	16:47:46	2005/08/23	0	200.9	12.4771	4949	2.9689
1	DMSW_standard	18-O_-23.23	2325	CO2	16:47:46	2005/08/23	0	250.6	11.3434	4507	2.9472
1	DMSW_standard	18-O_-23.23	2325	CO2	16:47:46	2005/08/23	0	300.3	10.2987	4080	3.151
1	DMSW_standard	18-O_-23.23	2325	CO2	16:47:46	2005/08/23	0	350	9.3472	3706	3.1067
1	DMSW_standard	18-O_-23.23	2325	CO2	16:47:46	2005/08/23	0	399.8	8.4734	3365	2.9519
1	DMSW_standard	18-O_-23.23	2325	CO2	16:47:46	2005/08/23	0	449.6	7.7022	3045	2.9671
1	DMSW_standard	18-O_-23.23	2325	CO2	16:47:46	2005/08/23	0	499.3	6.984	2764	3.2532
1	DMSW_standard	18-O_-23.23	2325	CO2	16:47:46	2005/08/23	0	549	6.3548	2512	3.0799
1	DMSW_standard	18-O_-23.23	2325	CO2	16:47:46	2005/08/23	0	598.7	5.7602	2273	3.1396
1	DMSW_standard	18-O_-23.23	2325	CO2	16:47:46	2005/08/23	0	648.4	5.2322	2065	3.2269
2	Dasani_standard	18-O_-7.99	2326	CO2	17:04:41	2005/08/23	1	35.1	80.0687	4047	0
2	Dasani_standard	18-O_-7.99	2326	CO2	17:04:41	2005/08/23	1	84.8	79.9318	4037	0
2	Dasani_standard	18-O_-7.99	2326	CO2	17:04:41	2005/08/23	1	132.2	80.2696	4063	0
2	Dasani_standard	18-O_-7.99	2326	CO2	17:04:41	2005/08/23	0	201	12.3826	4902	18.1593
2	Dasani_standard	18-O_-7.99	2326	CO2	17:04:41	2005/08/23	0	250.7	11.2391	4449	18.223
2	Dasani_standard	18-O_-7.99	2326	CO2	17:04:41	2005/08/23	0	300.4	10.1648	4029	18.1971

2) **Separate the results for the standards (example 18Onear zero, PNZ, and MSW) from the sample results. This is best done by sorting the data by identifier 1 then cutting the data for the standards and pasting it into a new worksheet.**

3) **In the "Standards" worksheet, sort data by "isref?" or by retention time.**

4) **Go to the section where the reference gas peaks are (they all have d18O or d2H of exactly zero). Scan through the peak amplitudes to ensure that they are all the same within about 100mV. Look in particular for very high or very low amplitudes. Once this is done, you can insert rows to separate this data from the rest. Trim off un-needed columns.**

Line	Identifier 1	Identifier 2	Rt	Ampl 44	d 18O/16O
3	18-O_nearzero	18-O_+4.09	201	4860	29.6631
3	18-O_nearzero	18-O_+4.09	250.8	4411	29.8341
3	18-O_nearzero	18-O_+4.09	300.4	3985	29.8291
3	18-O_nearzero	18-O_+4.09	350.2	3607	29.8315
3	18-O_nearzero	18-O_+4.09	399.9	3260	29.7138
3	18-O_nearzero	18-O_+4.09	449.6	2955	29.6096
3	18-O_nearzero	18-O_+4.09	499.4	2675	29.753
3	18-O_nearzero	18-O_+4.09	549.1	2421	29.8225
3	18-O_nearzero	18-O_+4.09	598.9	2193	29.923
3	18-O_nearzero	18-O_+4.09	648.5	1985	29.9675
15	18-O_nearzero	18-O_+4.09	201	4866	29.8082
15	18-O_nearzero	18-O_+4.09	250.7	4424	30.0401
15	18-O_nearzero	18-O_+4.09	300.5	4017	30.0637
15	18-O_nearzero	18-O_+4.09	350.2	3655	29.9652
15	18-O_nearzero	18-O_+4.09	399.9	3312	29.9738
15	18-O_nearzero	18-O_+4.09	449.7	3008	30.1082
15	18-O_nearzero	18-O_+4.09	499.4	2733	29.95
15	18-O_nearzero	18-O_+4.09	549.2	2480	29.9228

5) **For the remaining section, sort the data by identifier 1 → line number → retention time.**

6) **In two new columns, calculate the mean isotope ratio and standard deviation for each sample.**

7) **Scan over the standard deviations for anything that stands out relative to the rest. You are looking for big standard deviations relative to the rest.**

Line	Identifier 1	Identifier 2	Rt	Ampl 44	d 18O/16O	mean d18O	stdev
3	18-O_nearzero	18-O_+4.09	201	4860	29.6631		
3	18-O_nearzero	18-O_+4.09	250.8	4411	29.8341		
3	18-O_nearzero	18-O_+4.09	300.4	3985	29.8291		
3	18-O_nearzero	18-O_+4.09	350.2	3607	29.8315		
3	18-O_nearzero	18-O_+4.09	399.9	3260	29.7138		
3	18-O_nearzero	18-O_+4.09	449.6	2955	29.6096		
3	18-O_nearzero	18-O_+4.09	499.4	2675	29.753		
3	18-O_nearzero	18-O_+4.09	549.1	2421	29.8225		
3	18-O_nearzero	18-O_+4.09	598.9	2193	29.923		
3	18-O_nearzero	18-O_+4.09	648.5	1985	29.9675	29.79	0.11
15	18-O_nearzero	18-O_+4.09	201	4866	29.8082		
15	18-O_nearzero	18-O_+4.09	250.7	4424	30.0401		
15	18-O_nearzero	18-O_+4.09	300.5	4017	30.0637		
15	18-O_nearzero	18-O_+4.09	350.2	3655	29.9652		
15	18-O_nearzero	18-O_+4.09	399.9	3312	29.9738		
15	18-O_nearzero	18-O_+4.09	449.7	3008	30.1082		
15	18-O_nearzero	18-O_+4.09	499.4	2733	29.95		
15	18-O_nearzero	18-O_+4.09	549.2	2480	29.9228		
15	18-O_nearzero	18-O_+4.09	598.9	2252	30.0201		
15	18-O_nearzero	18-O_+4.09	648.6	2052	30.0797	29.99	0.09
27	18-O_nearzero	18-O_+4.09	201	4878	29.84		
27	18-O_nearzero	18-O_+4.09	250.7	4438	30.027		
27	18-O_nearzero	18-O_+4.09	300.4	4011	30.0288		
27	18-O_nearzero	18-O_+4.09	350.1	3637	30.0199		
27	18-O_nearzero	18-O_+4.09	399.9	3293	30.0974		
27	18-O_nearzero	18-O_+4.09	449.6	2981	30.1168		
27	18-O_nearzero	18-O_+4.09	499.4	2701	30.1487		
27	18-O_nearzero	18-O_+4.09	549.1	2450	29.9857		

8) **Open a new worksheet. Select all of the data in the "standards" worksheet and choose paste special → values to paste it into the new worksheet.**

9) **In the new worksheet, sort the data by the mean isotope ratio. This allows you to delete all of the other data. You should also delete all columns of data other than the one identifying the sample line number, the sample identifier, and the mean d18O.**

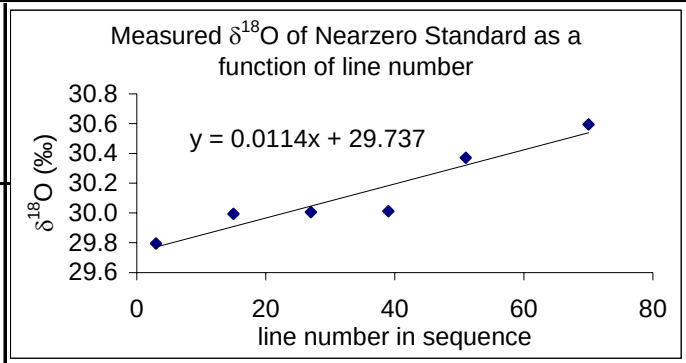
10) **Sort this data by identifier 1 and line number. These are your final, uncorrected results for the standards.**

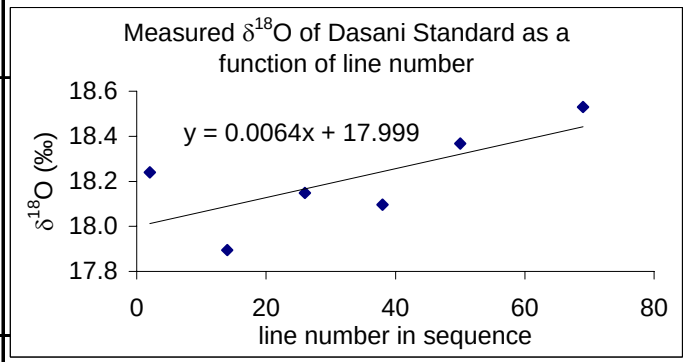
Line	Identifier 1	Identifier 2	mean d18O	stdev
3	18-O_nearzero	18-O_+4.09	29.79	0.11
15	18-O_nearzero	18-O_+4.09	29.99	0.09
27	18-O_nearzero	18-O_+4.09	30.01	0.11
39	18-O_nearzero	18-O_+4.09	30.01	0.10
51	18-O_nearzero	18-O_+4.09	30.37	0.09
70	18-O_nearzero	18-O_+4.09	30.60	0.11
		mean	30.13	
		stdev	0.29	
2	Dasani_standard	18-O_-7.99	18.24	0.09
14	Dasani_standard	18-O_-7.99	17.89	0.09
26	Dasani_standard	18-O_-7.99	18.15	0.10
38	Dasani_standard	18-O_-7.99	18.10	0.09
50	Dasani_standard	18-O_-7.99	18.37	0.06
69	Dasani_standard	18-O_-7.99	18.53	0.09
		mean	18.21	
		stdev	0.22	
1	DMSW_standard	18-O_-23.23	3.08	0.12
13	DMSW_standard	18-O_-23.23	2.79	0.08
25	DMSW_standard	18-O_-23.23	3.03	0.10
37	DMSW_standard	18-O_-23.23	2.95	0.06
49	DMSW_standard	18-O_-23.23	3.06	0.05
68	DMSW_standard	18-O_-23.23	3.38	0.08
		mean	3.05	
		stdev	0.19	

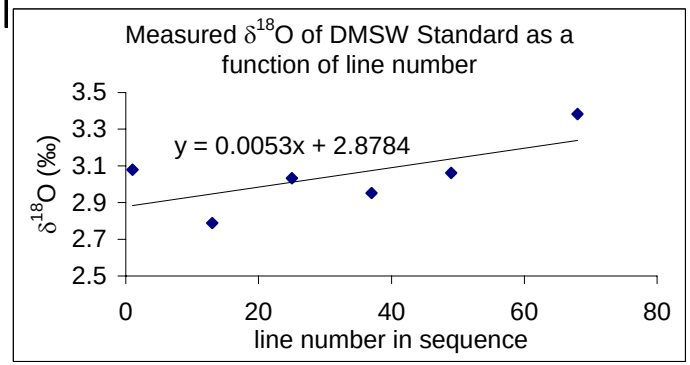
11) Plot the mean d18O as a function of the line number for each of the three standards. Look for anything that does not fit a trend. For example, single points that are significantly different from the rest. Any weirdness should be evident in all three plots. If there is anything strange, or you aren't sure, then talk to me (Anthony) about it right away. If I am not around then be sure to put your vials into a test tube rack in the same sequence that they are sitting on the heating block.

Line	Identifier 1	Identifier 2	mean d18O	stdev
3	18-O_nearzero	18-O_+4.09	29.79	0.11
15	18-O_nearzero	18-O_+4.09	29.99	0.09
27	18-O_nearzero	18-O_+4.09	30.01	0.11
39	18-O_nearzero	18-O_+4.09	30.01	0.10
51	18-O_nearzero	18-O_+4.09	30.37	0.09
70	18-O_nearzero	18-O_+4.09	30.60	0.11
		mean	30.13	
		stdev	0.29	
2	Dasani_standard	18-O_-7.99	18.24	0.09
14	Dasani_standard	18-O_-7.99	17.89	0.09
26	Dasani_standard	18-O_-7.99	18.15	0.10
38	Dasani_standard	18-O_-7.99	18.10	0.09
50	Dasani_standard	18-O_-7.99	18.37	0.06
69	Dasani_standard	18-O_-7.99	18.53	0.09
		mean	18.21	
		stdev	0.22	
1	DMSW_standard	18-O_-23.23	3.08	0.12
13	DMSW_standard	18-O_-23.23	2.79	0.08
25	DMSW_standard	18-O_-23.23	3.03	0.10
37	DMSW_standard	18-O_-23.23	2.95	0.06
49	DMSW_standard	18-O_-23.23	3.06	0.05
68	DMSW_standard	18-O_-23.23	3.38	0.08
		mean	3.05	
		stdev	0.19	

	Drift Slope
Nearzero	0.0114
Dasani	0.0064
DMSW	0.0053
mean	0.0077







The small slope for each of these plots show that there is a small amount of drift over time. As line number in the sequence is directly proportional to analysis time, we can make a drift correction based on the line number of the sample or standard.

Note: if the data is obviously not linear, then a polynomial fit can be used instead.

12) **Use the average slope of the three curves for your drift correction. Assuming the slope is 0.0029, then create a new column next to the one showing your results for the standards and call it "drift corrected". Then use the formula "=uncorrectednumber-linenumber*0.0029", where "uncorrectednumber" is the measured d18O for your standard. This assumes that the isotope ratio of the sample will increase by a small amount over time. Hence, you are subtracting out that increase.**

Line	Identifier 1	Identifier 2	mean d18O	stdev	Drift corrected
3	18-O_nearzero	18-O_+4.09	29.79	0.11	29.77
15	18-O_nearzero	18-O_+4.09	29.99	0.09	29.88
27	18-O_nearzero	18-O_+4.09	30.01	0.11	29.80
39	18-O_nearzero	18-O_+4.09	30.01	0.10	29.71
51	18-O_nearzero	18-O_+4.09	30.37	0.09	29.98
70	18-O_nearzero	18-O_+4.09	30.60	0.11	30.06
		mean	30.13		29.87
		stdev	0.29		0.13
2	Dasani_standard	18-O_-7.99	18.24	0.09	18.22
14	Dasani_standard	18-O_-7.99	17.89	0.09	17.79
26	Dasani_standard	18-O_-7.99	18.15	0.10	17.95
38	Dasani_standard	18-O_-7.99	18.10	0.09	17.80
50	Dasani_standard	18-O_-7.99	18.37	0.06	17.98
69	Dasani_standard	18-O_-7.99	18.53	0.09	18.00
		mean	18.21		17.96
		stdev	0.22		0.16
1	DMSW_standard	18-O_-23.23	3.08	0.12	3.07
13	DMSW_standard	18-O_-23.23	2.79	0.08	2.69
25	DMSW_standard	18-O_-23.23	3.03	0.10	2.84
37	DMSW_standard	18-O_-23.23	2.95	0.06	2.67
49	DMSW_standard	18-O_-23.23	3.06	0.05	2.68
68	DMSW_standard	18-O_-23.23	3.38	0.08	2.86
		mean	3.05		2.80
		stdev	0.19		0.16

Mean and stdev before the drift correction

Mean and stdev with the drift correction

The average slope from the three plots is used to correct the measured results for drift. This should ALWAYS result in better overall precision than without the correction. If that is not the case, then there may be no drift with the associated run, or the correction was not performed correctly.

	Drift Slope
Nearzero	0.0114
Dasani	0.0064
DMSW	0.0053
mean	0.0077

drift correction line: **y=meand18O-0.0077*linenumber**

13) **Make a new column called “known d18O” and put in the known value for the standards you used.**

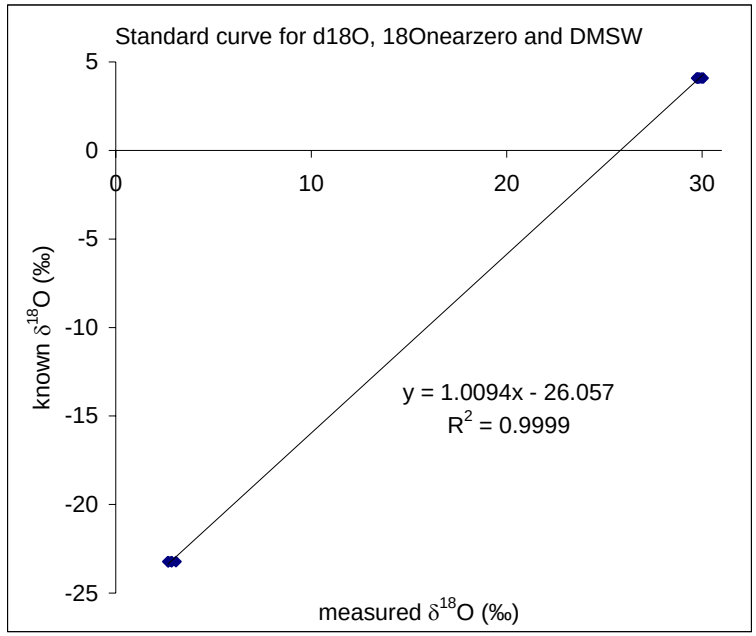
14) **Plot the known value as a function of the measured value. For the high and low standards. Label the axes x=measured $\delta^{18}O$ (‰) and y=known $\delta^{18}O$ (‰)**

15) **Insert a trend line and select the option that lets you see the equation of the line and the R^2 value. The equation of this line is the normalization curve for rescaling your sample results relative to VSMOW.**

Line	Identifier 1	Identifier 2	mean d18O	stdev	Drift corrected	known d18O
3	18-O_nearzero	18-O_+4.09	29.79	0.11	29.77	4.09
15	18-O_nearzero	18-O_+4.09	29.99	0.09	29.88	4.09
27	18-O_nearzero	18-O_+4.09	30.01	0.11	29.80	4.09
39	18-O_nearzero	18-O_+4.09	30.01	0.10	29.71	4.09
51	18-O_nearzero	18-O_+4.09	30.37	0.09	29.98	4.09
70	18-O_nearzero	18-O_+4.09	30.60	0.11	30.06	4.09
		mean	30.13		29.87	
		stdev	0.29		0.13	
2	Dasani_standard	18-O_-7.99	18.24	0.09	18.22	-7.99
14	Dasani_standard	18-O_-7.99	17.89	0.09	17.79	-7.99
26	Dasani_standard	18-O_-7.99	18.15	0.10	17.95	-7.99
38	Dasani_standard	18-O_-7.99	18.10	0.09	17.80	-7.99
50	Dasani_standard	18-O_-7.99	18.37	0.06	17.98	-7.99
69	Dasani_standard	18-O_-7.99	18.53	0.09	18.00	-7.99
		mean	18.21		17.96	
		stdev	0.22		0.16	
1	DMSW_standard	18-O_-23.23	3.08	0.12	3.07	-23.23
13	DMSW_standard	18-O_-23.23	2.79	0.08	2.69	-23.23
25	DMSW_standard	18-O_-23.23	3.03	0.10	2.84	-23.23
37	DMSW_standard	18-O_-23.23	2.95	0.06	2.67	-23.23
49	DMSW_standard	18-O_-23.23	3.06	0.05	2.68	-23.23
68	DMSW_standard	18-O_-23.23	3.38	0.08	2.86	-23.23
		mean	3.05		2.80	
		stdev	0.19		0.16	

	Drift Slope
Nearzero	0.0114
Dasani	0.0064
DMSW	0.0053
mean	0.0077

drift correction eqn.
y=meand18O-0.0077*linenumber



16) **Calculate the isotope ratio of the standards from this standard curve. Calculate the mean and standard deviation of these values. The "in between" standard is intended as a check of instrument linearity. It should come within two standard errors of the "known" value.**

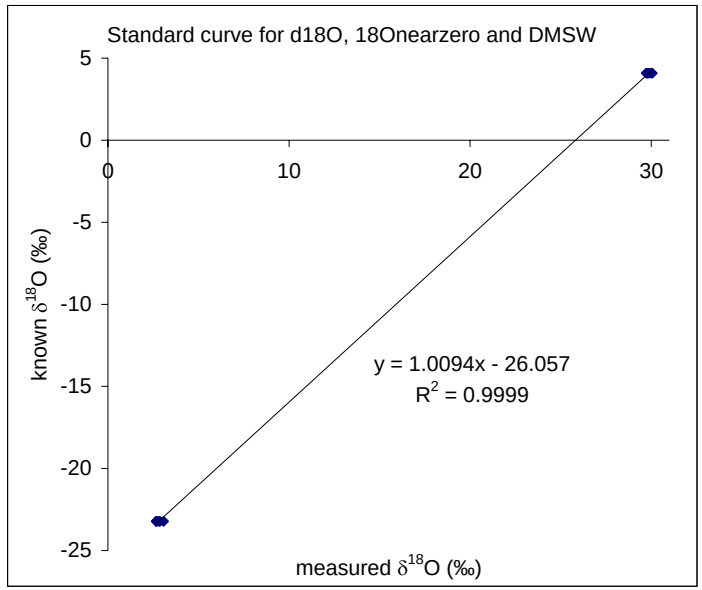
17) **Use the average value of the standard deviations of the standards as the analytical error for individual sample measurements.**

Line	Identifier 1	Identifier 2	mean d18O	stdev	Drift corrected	known d18O	calculated d18O
3	18-O_nearzero	18-O_+4.09	29.79	0.11	29.77	4.09	3.99
15	18-O_nearzero	18-O_+4.09	29.99	0.09	29.88	4.09	4.10
27	18-O_nearzero	18-O_+4.09	30.01	0.11	29.80	4.09	4.02
39	18-O_nearzero	18-O_+4.09	30.01	0.10	29.71	4.09	3.93
51	18-O_nearzero	18-O_+4.09	30.37	0.09	29.98	4.09	4.20
70	18-O_nearzero	18-O_+4.09	30.60	0.11	30.06	4.09	4.28
		mean	30.13		29.87	mean	**4.09**
		stdev	0.29		0.13	stdev	0.13
						sterr	0.05
2	Dasani_standard	18-O_-7.99	18.24	0.09	18.22	-7.99	-7.66
14	Dasani_standard	18-O_-7.99	17.89	0.09	17.79	-7.99	-8.10
26	Dasani_standard	18-O_-7.99	18.15	0.10	17.95	-7.99	-7.94
38	Dasani_standard	18-O_-7.99	18.10	0.09	17.80	-7.99	-8.09
50	Dasani_standard	18-O_-7.99	18.37	0.06	17.98	-7.99	-7.91
69	Dasani_standard	18-O_-7.99	18.53	0.09	18.00	-7.99	-7.89
		mean	18.21		17.96	mean	**-7.93**
		stdev	0.22		0.16	stdev	0.16
						sterr	0.07
1	DMSW_standard	18-O_-23.23	3.08	0.12	3.07	-23.23	-22.96
13	DMSW_standard	18-O_-23.23	2.79	0.08	2.69	-23.23	-23.34
25	DMSW_standard	18-O_-23.23	3.03	0.10	2.84	-23.23	-23.19
37	DMSW_standard	18-O_-23.23	2.95	0.06	2.67	-23.23	-23.37
49	DMSW_standard	18-O_-23.23	3.06	0.05	2.68	-23.23	-23.35
68	DMSW_standard	18-O_-23.23	3.38	0.08	2.86	-23.23	-23.17
		mean	3.05		2.80	mean	**-23.23**
		stdev	0.19		0.16	stdev	0.16
						sterr	0.06

	Drift Slope
Nearzero	0.0114
Dasani	0.0064
DMSW	0.0053
mean	0.0077

drift correction eqn.
y=meand18O-0.0077*linenumber

mean stdev for standards: **0.15**



18) **Sort the sample data in the same way as the standard data: separate the reference gas pulses out and inspect that they all have the same intensity to within +/-100mV. Put the sample data in a new sheet, sorted by identifier1 → line → Rt. Check that the intensity of each of the peaks decreases in a consistent way (ie. From 4800mV to 2000mV with no weird spikes). Chop out the extraneous columns of data.**

19) **Calculate the mean and standard deviation for each sample. Then copy over the equation for the drift correction and the equation for the standard curve. Make the drift correction on the sample mean, then use the standard curve to rescale the drift corrected value.**

Line	Identifier 1	Identifier 2	d 18O/16O	mean d18O	stdev	drift corrected	d18O vs VSMOW	
30	050717I	Stream 1 SW of GOPA	6.7679					
30	050717I	Stream 1 SW of GOPA	6.7934					
30	050717I	Stream 1 SW of GOPA	6.7873					
30	050717I	Stream 1 SW of GOPA	6.7428					drift correction eqn.
30	050717I	Stream 1 SW of GOPA	6.8192					y=meand18O-0.0077*linenumber
30	050717I	Stream 1 SW of GOPA	6.863					
30	050717I	Stream 1 SW of GOPA	6.8789					Standard curve
30	050717I	Stream 1 SW of GOPA	6.9806					y = 1.0094x - 26.057
30	050717I	Stream 1 SW of GOPA	6.8461					
30	050717I	Stream 1 SW of GOPA	6.8957	6.84	0.07	6.61	-19.39	
62	050717L	Vomit Pool	14.2726					
62	050717L	Vomit Pool	14.2398					
62	050717L	Vomit Pool	14.2535					
62	050717L	Vomit Pool	14.4319					
62	050717L	Vomit Pool	14.4543					
62	050717L	Vomit Pool	14.3655					
62	050717L	Vomit Pool	14.2375					
62	050717L	Vomit Pool	14.4537					
62	050717L	Vomit Pool	14.2577					
62	050717L	Vomit Pool	14.2828	14.32	0.09	13.85	-12.08	
31	050717M	Murkey Brown	17.9623					
31	050717M	Murkey Brown	17.9256					

18) **Sort the sample data in the same way as the standard data: separate the reference gas pulses out and inspect that they all have the same intensity to within +/-100mV. Put the sample data in a new sheet, sorted by identifier1 → line → Rt. Check that the intensity of each of the peaks decreases in a consistent way (ie. From 4800mV to 2000mV with no weird spikes). Chop out the extraneous columns of data.**

19) **Add in a section showing the drift correction and standard curve equations. Also include data showing the known and measured values for the standards. The "high" and "low" should exactly match their known values. The "in between" sample should be within two standard errors of its known value. Report the Standard Deviation for Samples as the average of the standard deviations measured for the standards.**

Line	Identifier 1	Identifier 2	d18O vs VSMOW
4	050719X	Flatcone	-16.97
5	050719Z	Evil Thought #3	-14.79
6	050719D	Four Eyes	-16.27
7	050719A	Special Dark	-11.67
8	050719B	Milk Chocolate	-11.86
9	050719F	Queens Laundry	-16.70
10	050721X	Meadow Stream	-14.10
11	050718X	Hot Shit Hill	-12.31
12	050718Y	Goose Lake Outflow	-10.98
16	050718I	Meadow Squeezings	0.14
17	050718J	Fudge Factory	-10.81
18	050718K	Lake NE of trail to GOPA	-2.29
19	050718C	Red Spot Three	-10.17
20	050718D	South Obsidian Pool	-14.59
21	050718E	Mars in a Bucket	-11.75
22	050718F	Brain Bog Upper	-12.70
23	050718G	Brain Bog Middle	-14.25
24	050718H	Brain Bog	-16.23
28	050719H	Stream 2 SW of GOPA	-17.29

Analytical Factors

drift correction eqn.
y=meand18O-0.0077*linenumber

Standard curve
y = 1.0094x - 26.057

Standards	known	mean	stdev	stderr
Nearzero	4.09	4.09	0.13	0.05
Dasani	**-7.99**	**-7.93**	**0.16**	**0.07**
DMSW	-23.23	-23.23	0.16	0.06

Standard Deviation for Samples: 0.15