U Isotopic Compositions and Concentrations of Rocky Flats Water Samples Collected Over the Period 4/1/15 to 6/16/15 and Submitted to LBNL

John N. Christensen

Data Report date 12/30/15

Twenty-one water samples were submitted by SM Stoller to Lawrence Berkeley National Laboratory (LBNL) for uranium (U) isotopic analysis. The sample set includes four composite samples from the WALPOC location, one composite sample from GS10, one composite sample from the SW093 location, and one sample each from wells 79102, 79302 and 79502. Analyses of previous samples from these locations were provided in earlier reports. The remaining 12 samples (both surface water and groundwater) are from locations not previously analyzed by LBNL. These samples were collected during the period from April 2015 through mid-June 2015 (see Table 1 for specific dates and periods).

METHODS:

U isotopic compositions of the samples were determined at LBNL by multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS; Neptune + model, manufactured by Thermo) on chemically separated U. All processes used high-purity reagents; new, never-used-before Teflon vials; and fresh separation resin. Details of the analytical processes are provided below.

Based on U concentrations provided or estimated by Stoller, aliquots from each sample were taken by volumetric pipette sufficient to yield 90 nanograms (ng) of U and transferred to new Teflon vials and dried down. After drying down, the samples were taken up in 8 N HNO_3 and re-dried. The samples were then taken up in 3 N HNO_3, centrifuged, and pipetted onto small-volume Teflon columns. Prior to sample introduction, the columns were filled with fresh UTEVA resin (Eichrom, Inc.) , and cleaned on the column with 0.05 M HCl, and then conditioned with 3 N HNO_3. (Prior to use, the resin was cleaned by repeated suspension, settling and decanting of supernate using deionized water.) After

sample loading, the columns were eluted with 3 N HNO_3 followed by 6 N HCL, and then U was rinsed from the columns and collected with 0.05 M HCl. After collection, a drop of concentrated $HClO_4$ was added, and the separate dried down in a perchloric hood. After the $HClO_4$ was driven off, a drop of concentrated HNO_3 was used to take up the U sample, and again dried down nearly to complete dryness. At this point, sufficient 0.3 N HNO_3 was added to bring up a solution of U at a concentration of 30 ppb. This is the solution that was used for MC-ICPMS analysis. Procedural blanks for U were much less than 0.1% of the sample size (i.e., <50 picogram [pg]). No ^{236}U was detectible in the procedural blank solution.

U isotopic compositions ($^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$) were measured on a Neptune + MC-ICPMS at LBNL. Uranium isotopes 235 and 238 were measured simultaneously on separate Faraday cups, while isotopes 234 and 236 were measured on a secondary electron multiplier SEM ion-counting system situated behind an energy filter. Two separate, static, and simultaneous measurement cycles were used: one for $^{235}U/^{238}U$ and $^{234}U/^{238}U$ and a second for $^{236}U/^{238}U$. Corrections for mass fractionation, SEM-Faraday inter-calibration, and any peak-tail under mass 236 were calculated from bracketed analyses of an in-house, secular equilibrium natural U standard (30 ppb solution of U ore from the Schwartzwalder Mine, CO provided by W. Sharp, Berkeley Geochronology Center). Isotopic compositions were normalized to the natural $^{238}U/^{235}U$ ratio (137.88 by convention [Steiger and Jäger, 1977]) of the standard solution using an exponential mass fractionation law. Sample solutions were introduced to the MC-ICPMS via a desolvation system (Apex IR, manufactured by ESI) equipped with a low-uptake micro-concentric nebulizer. Typical precision for $^{235}U/^{238}U$ is ±0.05% 2σ or better, and for $^{234}U/^{238}U$ and $^{236}U/^{238}U$ it is ±0.15% 2σ. $^{236}U/^{238}U$ can be measured down to the 10^{-7} range where precision degrades by approximately a factor of ten, with a minimum measurable ratio of $\sim 9 \times 10^{-8}$.

Using data from the Neptune taken during the isotopic analyses, the U concentration for each sample was estimated through a comparison of the size of the ^{238}U beam of the sample to the average ^{238}U beam size of the bracketing 30

ppb U isotopic standard. The concentrations given in Table 4 assume a 90% column yield based on yield tests.

RESULTS AND DISCUSSION:

The results of the U isotopic analyses are provided in Table 1, along with the U concentrations provided by Stoller from a contract lab. The isotopic data are also presented in Figures 1 and 2, and specifically for WALPOC samples in Figures 3 and 4. Calculated mass concentrations of ^{234}U, ^{235}U, ^{236}U, and ^{238}U (based on the measured isotopic compositions and provided contract lab U concentrations) are presented in Table 2. The percentages of presumed end-members (depleted U, enriched U, and natural U) were calculated using the Los Alamos National Laboratory (LANL) model spreadsheet and are provided in Table 3. The results of U concentration measurements from the contract lab and from LBNL (IsoProbe) are compared in Table 4 and are within an average of 13% of each other (for one sample, GS33 5/18/15-6/5/15, the LBNL U concentration is 41% low compared to the contract lab result; the rest are in the range of -22% to +29%).

Except for the case of groundwater sample 79102, all the remaining 20 samples analyzed for this report fall within the triangle defined by natural U, the LANL-defined depleted U, and enriched U end-members (Figure 1, shown at same scale as in previous reports). Both the current analysis of a sample from well 79102, and the analysis of a previous 79102 sample taken 5/14/12 yield similar U isotopic compositions (Table 5) that fall just outside the mixing triangle. This suggests that the model end-members don't completely capture the range of possible U isotopic compositions. (It may be that the "Depleted U" isotopic composition is not quite right. However, to preserve continuity with previous reports, the difference is not great enough to warrant a change in the model.)

The long-term (September 2011 to June 2015) changes in the U isotopic composition and concentration of WALPOC samples are shown as a set of time-series plots in Figure 4. The four most recent composite samples analyzed (this report- 3/26/15-4/7/15; 4/17/15-4/20/15; 5/18/15-5/26/15; 6/8/15-6/12/15) show a trend of decreasing U concentration, while at the same time

show a trend of increasing $^{235}U/^{238}U$ and $^{236}U/^{238}U$ to levels not seen in earlier portions of the record. With these trends, are trends in increasing proportions of the Depleted U and Enriched U end-members, and decreasing proportion of Natural U (Figure 4). In Figure 3, the WALPOC data are presented as $^{236}U/^{238}U$ vs. $^{235}U/^{238}U$; as noted in previous reports, WALPOC samples taken between September 2011 and February 2014 form a cluster. The WALPOC composite samples representing the periods 5/18/15-5/26/15 and 6/8/15-6/12/15 fall away from this cluster toward the direction of increasing proportion of the Enriched U end-member, and roughly toward the compositions of composite surface water samples taken at GS13 and SW093, and samples taken from wells 79402 and P210189 (P210189 falls closest to a line extending from WALPOC 4/17/15-4/20/15 through WALPOC 5/18/15-5/26/15 and 6/8/15-6/12/15) (see Figures 1 and 3). These observations suggest a shift in the balance of U sources contributing to U at WALPOC during the period covered by 4/17/15-4/20/15 and 5/18/15-5/26/15. The WALPOC composite sample taken over 6/8/15-6/12/15 suggests a shift back to the previous range in the balance of sources represented by the WALPOC cluster (Figure 3 and Figure 4).

The composite sample taken from 5/19/15-5/26/15 at location GS10 has a U isotopic composition similar to previous samples (see Table 5 for a comparison between the sample analyzed in this report, and its immediate predecessor given in the previous report) and suggests little change in the balance of the U sources.

Samples taken at SW093 approximately 7 months apart, show a distinct change in U isotopic composition with a shift towards a greater proportion of Enriched and Depleted U. The latest SW093 sample has a similar U isotopic composition to the GS13 sample taken over the same time period, and both are similar to the SPIN sample taken 6/16/15 that has a higher U concentration than the GSW13 and SW093 consistent with those samples being diluted SPIN water. In turn, the U isotopic composition of the SPIN sample suggests it was influenced by an up-gradient source of U such as represented by the current 79402 and P210189 samples.

The groundwater samples analyzed for this report provide a wider range of U isotopic compositions than seen in previous LBNL reports. The sample from well P210189, with a $^{236}U/^{238}U$ x10^6 of 102 and a $^{235}U/^{238}U$ of 0.02173 (Table 1) has the greatest fraction of Enriched U (1.6%, Table 3) though it has a modest U concentration of 43 ppb. In contrast, the sample from well 79605 has a U concentration of 550 ppb, but has a $^{235}U/^{238}U$ indistinguishable from Natural U, and a $^{236}U/^{238}U$ below detection (<9x10^8). The other groundwater sample with U isotopic compositions indistinguishable from Natural U is from well 00203. Surface water samples from the GS33 location (at the downstream end of No Name Gulch, just above its confluence with Walnut Creek) have low $^{236}U/^{238}U$ ratios of 0.5x10^6 (5/18/15-6/5/15) and 0.44x10^6 (3/9/15-4/1/15) and near-natural $^{238}U/^{235}U$ ratios of 138.298 (5/18/15-6/5/15) and 138.304 (3/9/15-4/1/15).

Reference

Steiger, R.H. and Jäger, E. (1977). Subcommission on geochronology: Convention on the use of decay constants in geo- and cosmochronology. *Earth Planet. Sci. Lttrs*. V.36, pp.359-362.

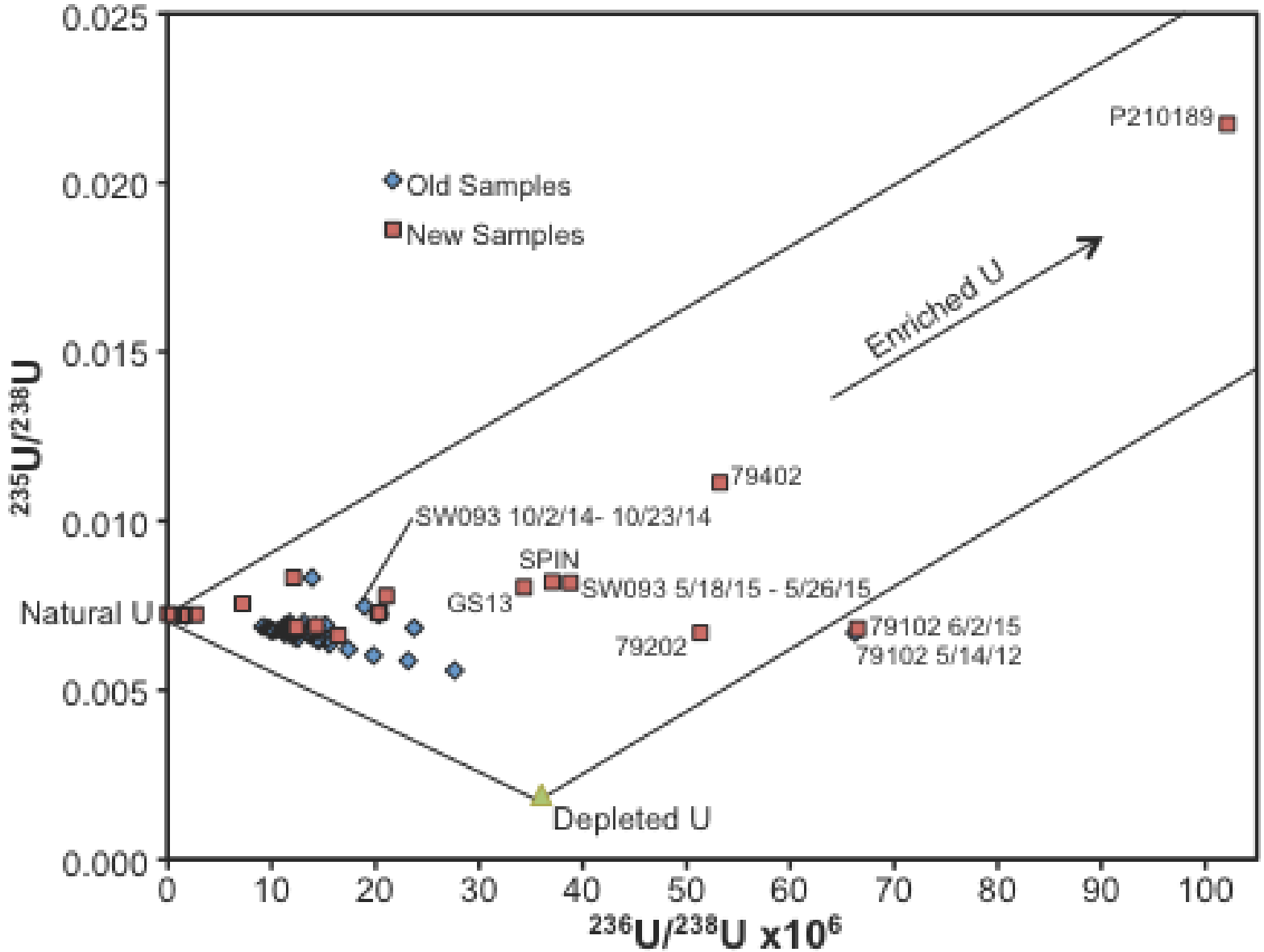

Figure 1. A comparison of samples analyzed for previous reports (blue diamonds) and samples for this report. Shown is the field defined by the end-members "Enriched U," "Depleted U," and "Natural U."

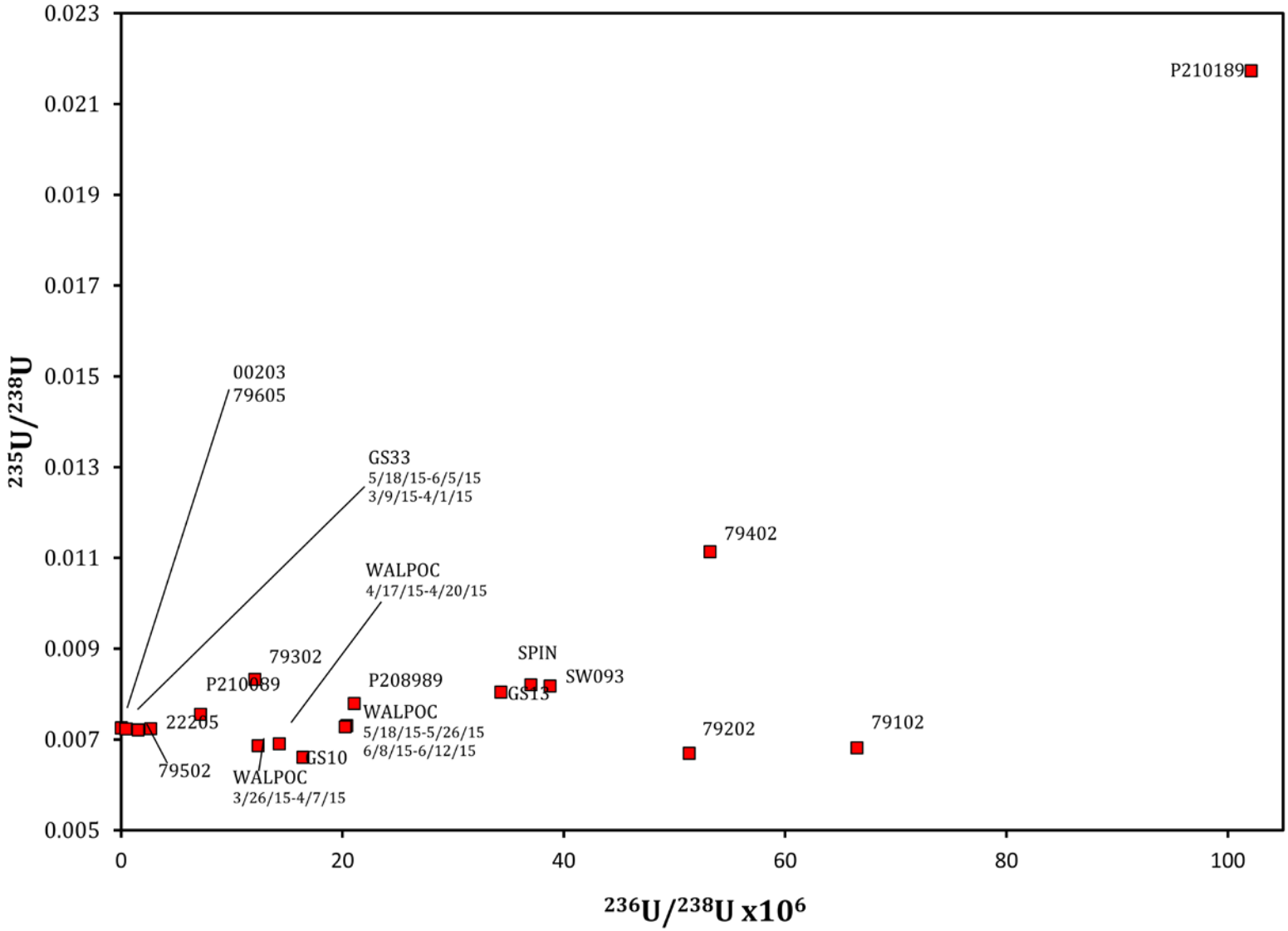

Figure 2. Plotted are data for the current batch of samples (4/1/15 to 6/16/15).

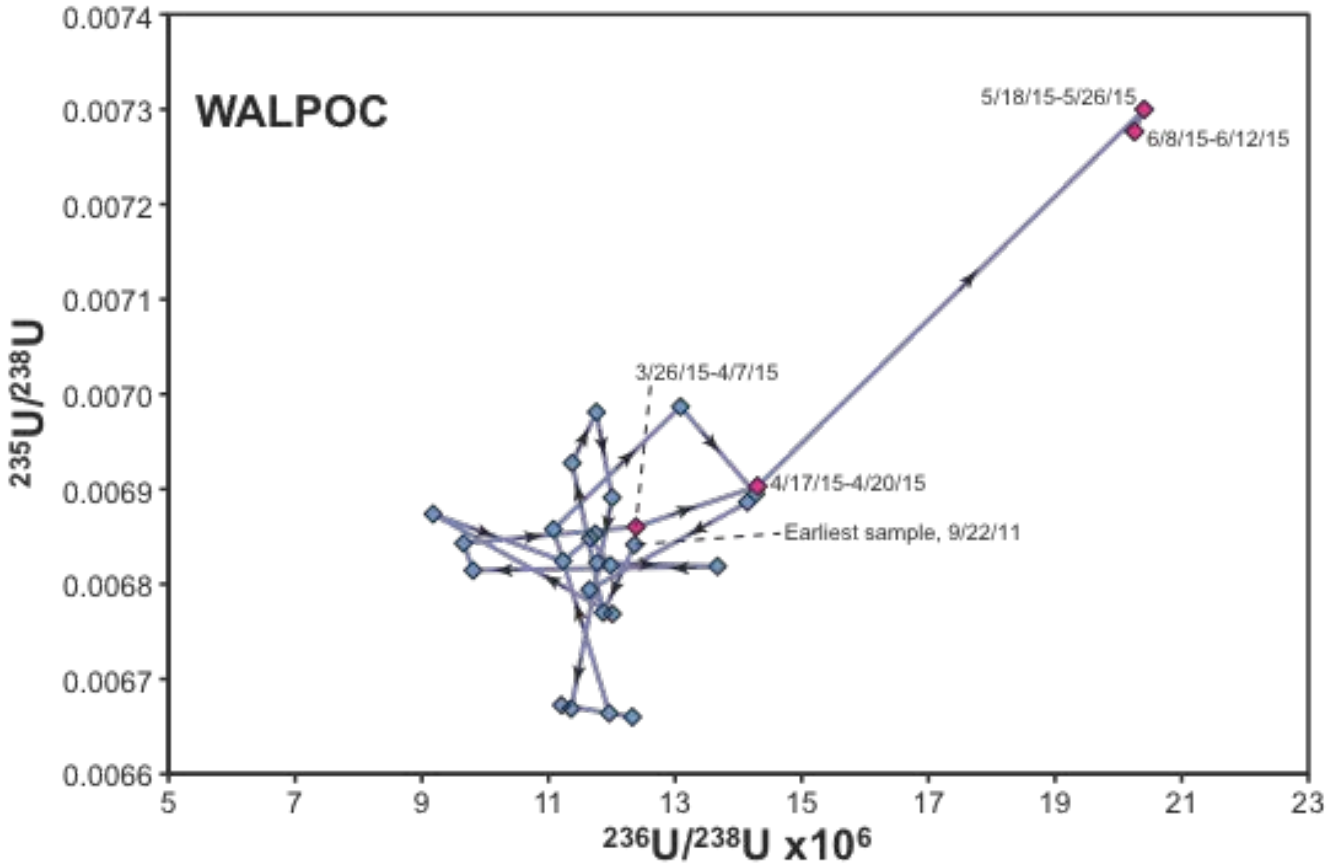

Figure 3. A plot of $^{236}U/^{238}U$ *vs.* $^{235}U/^{238}U$ for WALPOC samples taken since 9/22/11. Lines connect samples in sequence with arrows pointing forward in time. The red symbols are WALPOC samples analyzed for this report.

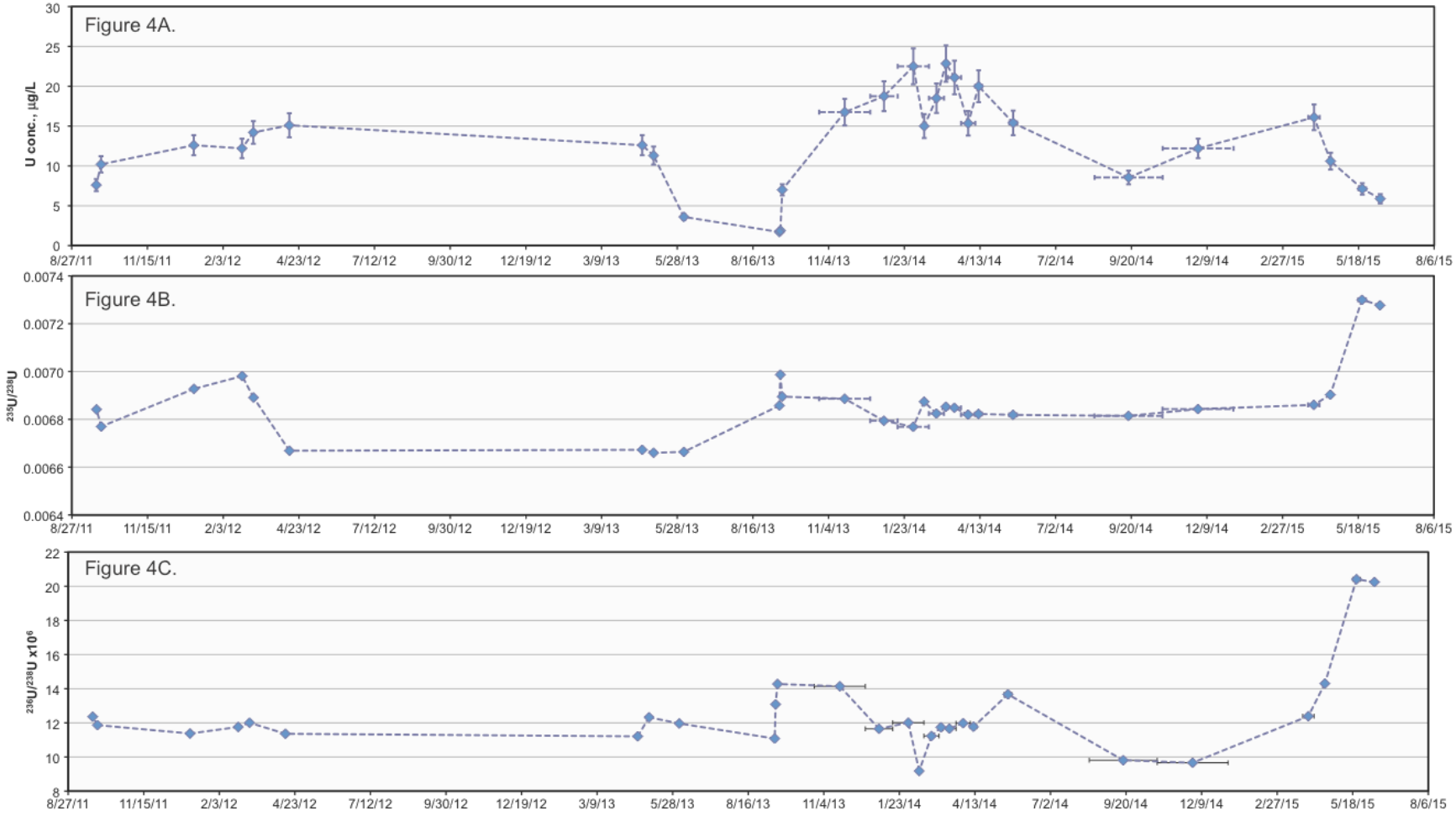
Figure 4A.
U conc., µg/L
30
25
20
15
10
5
0
8/27/11
11/15/11
2/3/12
4/23/12
7/12/12
9/30/12
12/19/12
3/9/13
5/28/13
8/16/13
11/4/13
1/23/14
4/13/14
7/2/14
9/20/14
12/9/14
2/27/15
5/18/15
8/6/15
Figure 4B.
235U/238U
0.0074
0.0072
0.0070
0.0068
0.0066
0.0064
Figure 4C.
236U/235U x10^6
22
20
18
16
14
12
10
8

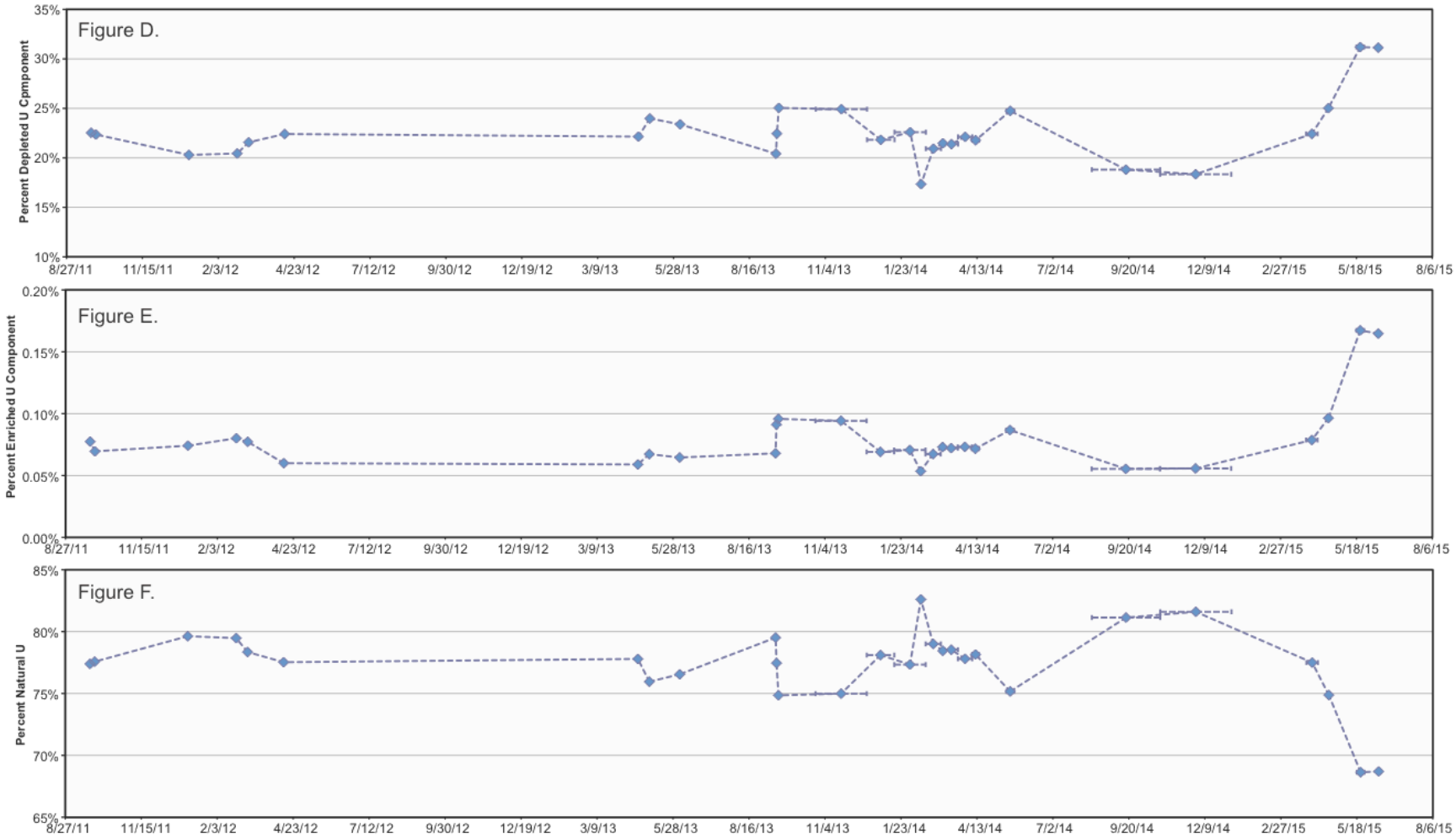

Figure 4 WALPOC time series of samples illustrating the variation with time of U isotopic composition. Note: Time spans of composite samples are represented by horizontal bars, in some cases smaller than the data symbols.

Table 1. U isotopic compositions and U concentrations

Sample Location	Sample Date(s)	Type	Total U‡ (ug/L)	$^{234}U/^{238}U$ x1e6	±2s abs	$^{238}U/^{235}U$	±2s abs	$^{235}U/^{238}U$	±2s abs	$^{236}U/^{238}U$ x1e6	±2s abs
79102	6/2/15	Groundwater	530	62.57	0.19	146.745	0.082	0.0068146	0.0000038	66.50	0.19
00203	5/27/15	Groundwater	130	70.25	0.11	137.875	0.064	0.0072530	0.0000034	<0.09	------
79302	6/2/15	Groundwater	220	91.64	0.11	120.177	0.062	0.0083211	0.0000043	12.11	0.11
79402	5/28/15	Groundwater	290	110.20	0.11	89.831	0.061	0.0111320	0.0000076	53.24	0.11
79605	5/27/15	Groundwater	550	69.25	0.06	137.897	0.078	0.0072518	0.0000041	<0.09	------
P208989	5/28/15	Groundwater	130	88.80	0.07	128.382	0.064	0.0077893	0.0000039	21.06	0.05
22205	6/2/15	Groundwater	43	73.16	0.06	138.251	0.076	0.0072332	0.0000040	2.67	0.05
P210089	5/28/15	Groundwater	27	77.48	0.05	132.407	0.078	0.0075525	0.0000044	7.19	0.05
79202	6/2/15	Groundwater	40	64.97	0.04	149.419	0.082	0.0066926	0.0000037	51.34	0.04
SPIN	6/16/15	Groundwater	78	81.51	0.04	121.941	0.082	0.0082007	0.0000055	37.03	0.04
79502	5/27/15	Groundwater	16	108.40	0.04	138.696	0.082	0.0072100	0.0000043	1.55	0.04
P210189	5/28/15	Groundwater	43	222.25	0.11	46.018	0.082	0.0217307	0.0000387	102.13	0.06
WALPOC	3/26/15-4/7/15	Surface Water	16.1	65.14	0.03	145.764	0.079	0.0068604	0.0000037	12.39	0.02
WALPOC	4/17/15-4/20/15	Surface Water	10.6	64.79	0.04	144.864	0.083	0.0069030	0.0000040	14.30	0.03
WALPOC	5/18/15-5/26/15	Surface Water	7.12	68.45	0.04	136.989	0.083	0.0072999	0.0000044	20.41	0.04
WALPOC	6/8/15-6/12/15	Surface Water	5.88	68.21	0.04	137.420	0.083	0.0072769	0.0000044	20.25	0.04
GS10	5/19/15-5/26/15	Surface Water	8.92	58.95	0.02	151.381	0.079	0.0066059	0.0000034	16.44	0.02
GS33	5/18/15-6/5/15	Surface Water	2.3	67.45	0.04	138.298	0.084	0.0072307	0.0000044	0.50	0.03
GS33	3/9/15-4/1/15	Surface Water	7.36	68.74	0.02	138.304	0.079	0.0072304	0.0000041	0.44	0.01
GS13	5/18/15-5/26/15	Surface Water	5.24	76.14	0.04	124.394	0.083	0.0080390	0.0000054	34.32	0.04
SW093	5/18/15-5/26/15	Surface Water	5.71	77.40	0.04	122.281	0.084	0.0081779	0.0000056	38.78	0.04

Notes: ±2s abs = two times the standard deviation in absolute terms.

‡Concentrations from contract lab (See Table 4 for LBNL U concentrations)

Table 2. Concentrations of U isotopes in samples

Sample Location	Sample Date(s)	^{234}U µg/L	^{235}U µg/L	^{236}U µg/L	^{238}U µg/L
79102	6/2/15	3.2E-02	3.5E+00	3.5E-02	526.3
00203	5/27/15	8.9E-03	9.2E-01	<7E-06	129.1
79302	6/2/15	2.0E-02	1.8E+00	2.6E-03	218.2
79402	5/28/15	3.1E-02	3.2E+00	1.5E-02	286.8
79605	5/27/15	3.7E-02	3.9E+00	<8E-06	546.0
P208989	5/28/15	1.1E-02	9.9E-01	2.7E-03	129.0
22205	6/2/15	3.1E-03	3.0E-01	1.1E-04	42.7
P210089	5/28/15	2.0E-03	2.0E-01	1.9E-04	26.8
79202	6/2/15	2.5E-03	2.6E-01	2.0E-03	39.7
SPIN	6/16/15	6.2E-03	6.3E-01	2.8E-03	77.4
79502	5/27/15	1.7E-03	1.1E-01	2.4E-05	15.9
P210189	5/28/15	9.2E-03	9.0E-01	4.3E-03	42.1
WALPOC	3/26/15-4/7/15	1.0E-03	1.1E-01	2.0E-04	16.0
WALPOC	4/17/15-4/20/15	6.7E-04	7.2E-02	1.5E-04	10.5
WALPOC	5/18/15-5/26/15	4.8E-04	5.1E-02	1.4E-04	7.1
WALPOC	6/8/15-6/12/15	3.9E-04	4.2E-02	1.2E-04	5.8
GS10	5/19/15-5/26/15	5.1E-04	5.8E-02	1.4E-04	8.9
GS33	5/18/15-6/5/15	1.5E-04	1.6E-02	1.1E-06	2.3
GS33	3/9/15-4/1/15	4.9E-04	5.2E-02	3.2E-06	7.3
GS13	5/18/15-5/26/15	3.9E-04	4.1E-02	1.8E-04	5.2
SW093	5/18/15-5/26/15	4.3E-04	4.6E-02	2.2E-04	5.7

Table 3. Percentages of end-members calculated using the LANL model

Sample Location	Sample Date(s)	Depleted	Enriched	Natural
79102	6/2/15	100.00%	0.51%	-0.51%
00203	5/27/15	<0.07%	0.00%	>99.93%
79302	6/2/15	9.90%	0.16%	89.95%
79402	5/28/15	50.29%	0.64%	49.07%
79605	5/27/15	<0.03%	0.00%	>99.97%
P208989	5/28/15	28.16%	0.20%	71.64%
22205	6/2/15	4.30%	0.02%	95.68%
P210089	5/28/15	8.65%	0.07%	91.27%
79202	6/2/15	84.08%	0.38%	15.53%
SPIN	6/16/15	49.46%	0.35%	50.19%
79502	5/27/15	2.75%	0.01%	97.24%
P210189	5/28/15	38.26%	1.61%	60.13%
WALPOC	3/26/15-4/7/15	22.42%	0.08%	77.50%
WALPOC	4/17/15-4/20/15	25.03%	0.10%	74.88%
WALPOC	5/18/15-5/26/15	31.20%	0.17%	68.64%
WALPOC	6/8/15-6/12/15	31.13%	0.16%	68.70%
GS10	5/19/15-5/26/15	30.79%	0.10%	69.11%
GS33	5/18/15-6/5/15	0.96%	0.00%	99.04%
GS33	3/9/15-4/1/15	0.87%	0.00%	99.12%
GS13	5/18/15-5/26/15	46.61%	0.32%	53.07%
SW093	5/18/15-5/26/15	52.36%	0.36%	47.28%

Table 4. Total U concentrations (μg/L), comparing contract lab to LBNL

Sample Location	Sample Date(s)	Contract Lab	LBNL	LBNL/Contract Percent
79102	6/2/15	530	517.1	98%
00203	5/27/15	130	102.0	78%
79302	6/2/15	220	226.9	103%
79402	5/28/15	290	296.0	102%
79605	5/27/15	550	583.3	106%
P208989	5/28/15	130	128.0	98%
22205	6/2/15	43	35.0	81%
P210089	5/28/15	27	26.3	97%
79202	6/2/15	40	51.5	129%
SPIN	6/16/15	78	76.1	98%
79502	5/27/15	16	14.6	91%
P210189	5/28/15	43	38.7	90%
WALPOC	3/26/15-4/7/15	16.1	14.2	88%
WALPOC	4/17/15-4/20/15	10.6	9.2	87%
WALPOC	5/18/15-5/26/15	7.12	5.7	79%
WALPOC	6/8/15-6/12/15	5.88	4.6	78%
GS10	5/19/15-5/26/15	8.92	7.4	83%
GS33	5/18/15-6/5/15	2.3	1.4	59%
GS33	3/9/15-4/1/15	7.36	6.6	90%
GS13	5/18/15-5/26/15	5.24	6.0	115%
SW093	5/18/15-5/26/15	5.71	5.2	92%

Table 5. Comparison of samples from locations analyzed for this report with those in previous reports

Sample Location	Sample Date(s)	Type	Total U‡ (ug/L)	$^{234}U/^{238}U$ x1e6	±2s abs	$^{238}U/^{235}U$	±2s abs	$^{235}U/^{238}U$	±2s abs	$^{236}U/^{238}U$ x1e6	±2s abs
79102	6/2/15	Groundwater	530	62.57	0.19	146.745	0.082	0.0068146	0.0000038	66.50	0.19
79102	5/14/12		510	60.85	0.1	149.398	0.075	0.0066935	0.0000034	66.26	0.06
79302	6/2/15	Groundwater	220	91.64	0.11	120.177	0.062	0.0083211	0.0000043	12.11	0.11
79302	10/29/13		183	91.55	0.14	120.224	0.08	0.0083178	0.0000055	13.89	0.03
79502	5/27/15	Groundwater	16	108.40	0.04	138.696	0.082	0.0072100	0.0000043	1.55	0.04
79502	10/29/13		11	97.51	0.14	138.844	0.082	0.0072023	0.0000043	1.79	0.02
SW093	5/18/15-5/26/15	Surface Water	5.7	77.40	0.04	122.281	0.084	0.0081779	0.0000056	38.78	0.04
SW093	10/2/14-11/19/14		4.7	72.47	0.10	133.706	0.150	0.0074791	0.0000084	18.96	0.10
GS10	5/19/15-5/26/15	Surface Water	8.92	58.95	0.02	151.381	0.079	0.0066059	0.0000034	16.44	0.02
GS10	10/2/14-10/23/14		10.6	61.48	0.12	153.130	0.088	0.0065304	0.0000038	12.47	0.10

Notes: ±2s abs = two times the standard deviation in absolute terms.