U Isotopic Compositions and Concentrations of the First Batch of Rocky Flats Water Samples Submitted to LBNL

John N. Christensen

Report date 9/16/13

Thirteen samples were submitted by SM Stoller to Lawrence Berkeley National Laboratory for uranium isotopic and concentration analysis- 12 surface water samples from two sites (WALPOC and GS10) covering the period Sept. 2011 to April 2013, and one groundwater sample taken on 5/14/12 from well 79102 (Table 1).

Uranium isotopic compositions of the samples were determined at LBNL by MC-ICPMS (IsoProbe, Mfd. by Micromass) 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 by Stoller, aliquots from each sample were taken by volumetric pipette sufficient to yield 90 ng of uranium and transferred to new Teflon vials and dried down. After drying down, the samples were taken up in 8N HNO3 and re-dried. The samples were then taken up in 1.5 N HNO3, centrifuged and pipetted onto small volume Teflon columns filled with TRU resin (Eichrom, Inc.). Prior to sample introduction, the columns were filled with fresh TRU resin, and cleaned with 0.2 M HCl and 0.3 M HF; and then conditioned with 1.5 N HNO3. After sample loading, the columns were eluted with 1.5 N HNO3, and then U was rinsed from the columns and collected with 0.5 N HF. After collection, a drop of HClO4 was added, and the separate dried down in a perchloric hood. After the HClO4 was driven off, a drop of concentrated HNO3 was used to take up the U sample, and again dried down nearly to complete dryness. At this point, sufficient 0.3 N HNO3 was added to bring up a solution of U at a concentration of 30 ppb. This is the solution that was used for mass spectrometry. Procedural blank for U were much less than 0.1% of the sample size (i.e. <50 pg). No ^{236}U was detectible in the procedural blank solution.

Uranium isotopic compositions ($^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$) were measured on an IsoProbe (MC-ICPMS) at. Uranium isotopes 235 and 238 were measured simultaneously on separate Faraday cups, while 234 and 236 were measured on a Daly ion counting system situated behind a wide-angle retardation potential lens. Two separate static simultaneous measurement routines 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, Daly-Faraday inter-calibration and for any peak-tail under mass 236 were calculated from bracketed analyses of an in-house secular equilibrium natural uranium 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 (Aridus II manufactured by CETAC Inc.) equipped with a low uptake micro-concentric nebulizer. Typical precision for $^{235}U/^{238}U$ is ±0.05% 2σ or better, for $^{234}U/^{238}U$ and $^{236}U/^{238}U$ it is ±0.15% 2σ. $^{236}U/^{238}U$ can be measured down to and below the 10^{-7} range where precision degrades by about a factor of ten with a minimum measurable ratio of $\sim 5 \times 10^{-8}$.

Uranium and Strontium concentrations were determined on separate 2 ml sample aliquots using quadrupole ICMP-MS (Perkin Elmer SCIEX Elan DRC II) using a four-standard concentration calibration and an internal check through spiking each sample with Ga to a known concentration.

The results of the U isotopic analyses, and the U and Sr concentration determinations are provided in Table 1. The data is also presented in Figures 1 and 2. Calculated mass concentrations of ^{234}U, ^{235}U, ^{236}U and ^{238}U based on the measured isotopic compositions and U concentrations (measured at LBNL) are presented in Table 2. The percentages of presumed end-members (depleted U, enriched U and natural U) were calculated using the Los Alamos model spreadsheet and are provided in Table 3.

Surface water samples taken at WALPOC show little U isotopic variation over the period September 2011 to May 2013, while over a similar period the four samples from GSO10 describe a much greater range that appears to be systematic reflecting variable mixtures of natural and contaminant U (dominated by depleted U) that is not consistent with the groundwater U composition from well 79102 (Fig. 1). Plotting the inverse of the U concentration against $^{236}U/^{238}U$ ratios (Fig. 2) suggests that in the case of the WALPOC samples, variation of U concentration is due to simple dilution (e.g. rainwater with virtually zero U), though loss of U due to mineral (e.g. carbonate) precipitation is also possible and can't be ruled out without further geochemical information. A plot of the inverse of Sr concentration against $^{236}U/^{238}U$ gives a very similar pattern (Fig. 3). It may be interesting to try $^{87}Sr/^{86}Sr$ as a supplementary tracer. For the four surface water samples from GS10, Fig. 2 and Fig. 3 suggests mixing between a natural U source (or a WALPOC endmember) and an emdmember consisting mainly of depleted U and a small fraction of enriched U, though not apparently corresponding to the groundwater sample from 79102.

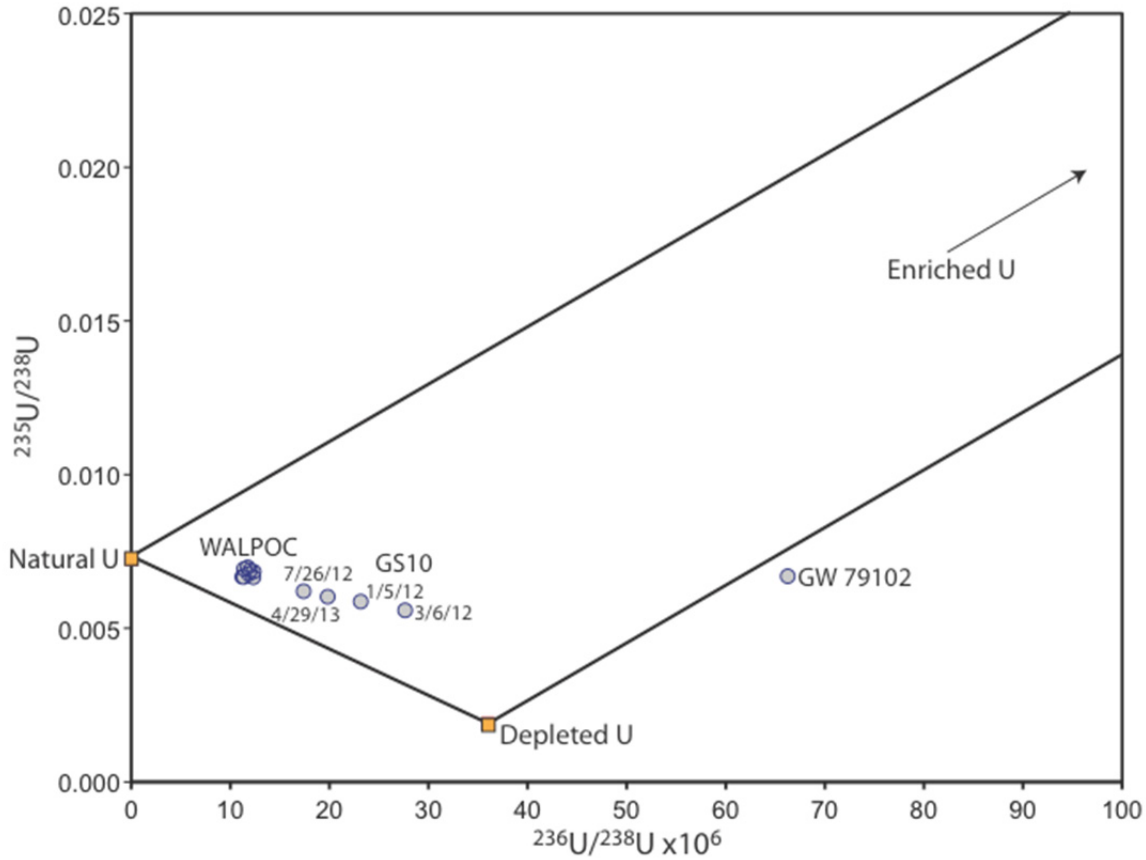
0.025
0.020
0.015
0.010
0.005
0.000
235U/238U
Enriched U
Natural U
WALPOC
GS10
7/26/12
1/5/12
4/29/13
3/6/12
GW 79102
Depleted U
0
10
20
30
40
50
60
70
80
90
100
236U/238U x10^6

Figure 1

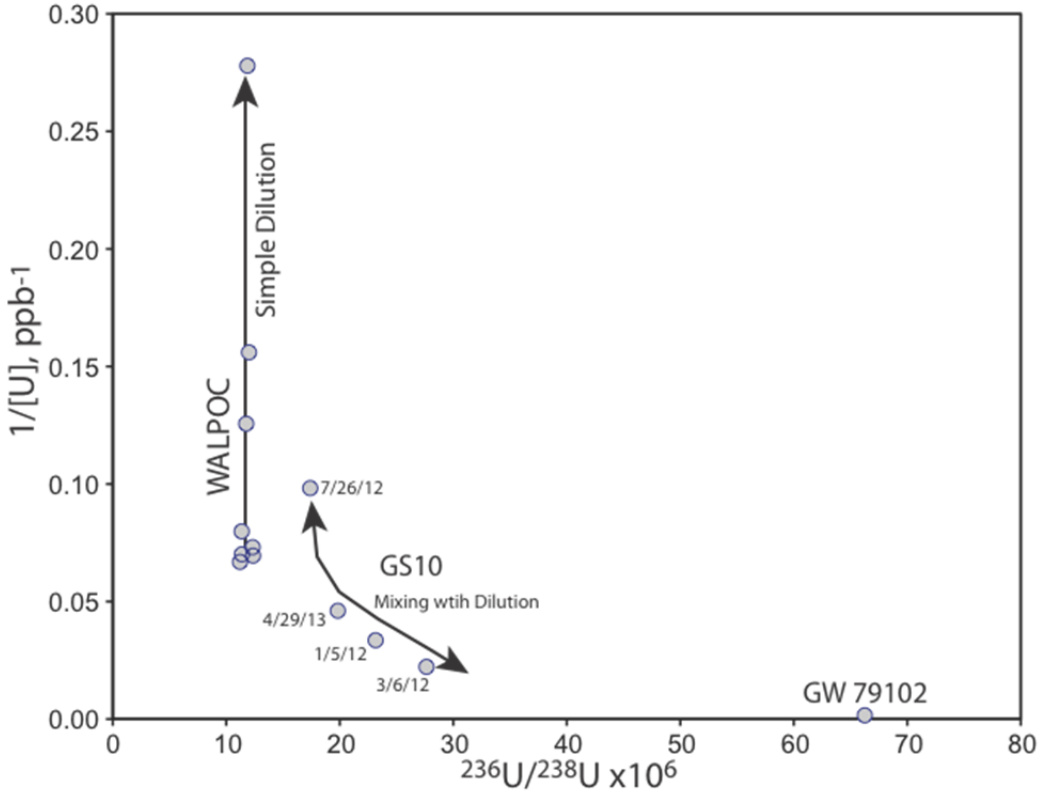

Figure 2.

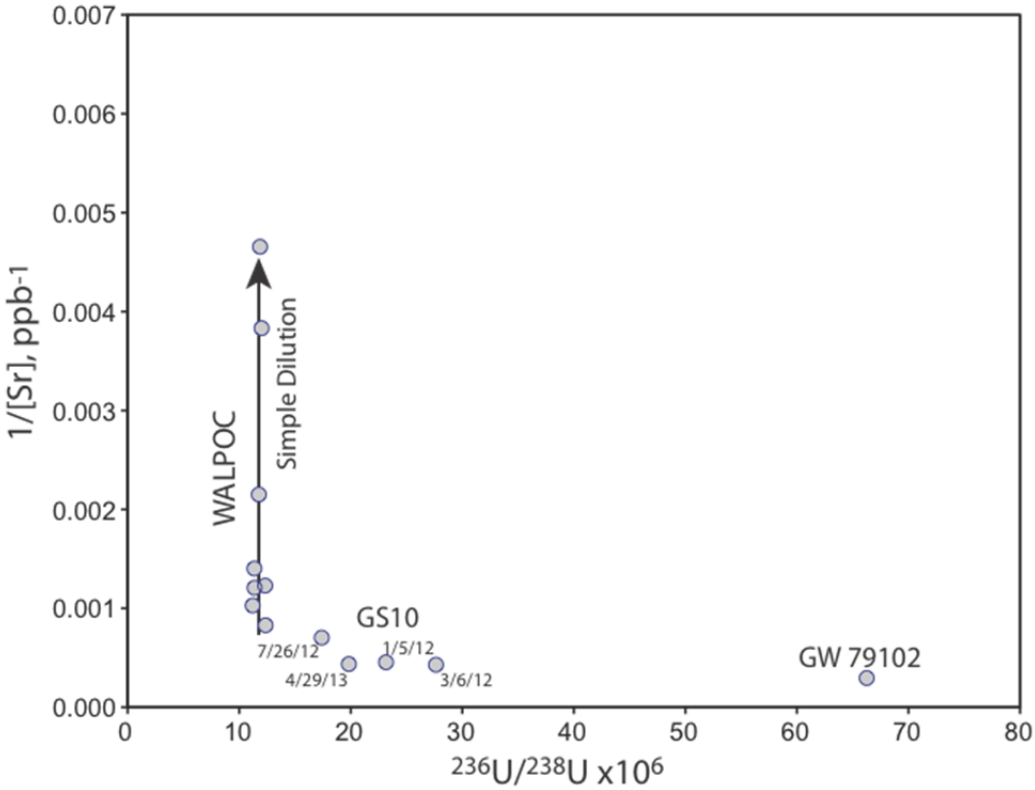

Figure 3.

Table 1. U isotopic compositions, U and Sr concentrations

Sample Location	Sample Date	Total U (ug/L)	Uncert.	Sr, ppb	$^{234}U/^{238}u$ x1e6	±2s abs	$^{238}U/^{235}U$	±2s abs	$^{235}U/^{238}U$	±2s abs	$^{236}U/^{238}U$ x1e6	±2s abs
WALPOC	9/22/11	14.4	0.3	1206.6	64.88	0.11	146.166	0.1	0.0068415	0.0000047	12.36	0.057
WALPOC	9/27/11	3.6	0.1	214.8	64.38	0.14	147.711	0.2	0.0067700	0.0000092	11.866	0.036
WALPOC	1/3/12	14.3	0.3	827.7	65.84	0.12	144.353	0.07	0.0069275	0.0000034	11.375	0.057
WALPOC	2/23/12	8.0	0.3	465.0	66.23	0.1	143.245	0.07	0.0069810	0.0000034	11.757	0.026
WALPOC	3/6/12	6.4	0.2	261.0	65.51	0.13	145.114	0.2	0.0068911	0.0000095	12.005	0.039
WALPOC	4/13/12	12.5	0.3	713.0	62.85	0.12	149.952	0.100	0.0066688	0.0000044	11.359	0.034
WALPOC	4/21/13	15.0	0.3	972.5	62.82	0.09	149.867	0.08	0.0066726	0.0000036	11.208	0.056
WALPOC	5/3/13	13.7	0.3	813.2	62.82	0.09	150.149	0.12	0.0066601	0.0000053	12.325	0.024
GS10	1/5/12	29.8	1.0	2198.8	52.82	0.11	170.395	0.150	0.0058687	0.0000052	23.162	0.048
GS10	3/6/12	45.0	1.5	2327.8	49.53	0.11	179.077	0.100	0.0055842	0.0000031	27.64	0.043
GS10	7/26/12	10.2	0.2	1421.4	57.31	0.1	161.159	0.15	0.0062051	0.0000058	17.395	0.06
GS10	4/29/13	21.7	0.8	2289.7	55.23	0.13	165.956	0.07	0.0060257	0.0000025	19.828	0.055
79102	5/14/12	623	22	3386.0	60.85	0.1	149.398	0.075	0.0066935	0.0000034	66.256	0.059

Table 2. Concentrations of U isotopes in samples

Sample Location	Sample Date	^{234}U µg/L	^{235}U µg/L	^{236}U µg/L	^{238}U µg/L
WALPOC	9/22/11	9.1E-04	9.7E-02	1.8E-04	14.3
WALPOC	9/27/11	2.3E-04	2.4E-02	4.2E-05	3.6
WALPOC	1/3/12	9.2E-04	9.7E-02	1.6E-04	14.2
WALPOC	2/23/12	5.1E-04	5.4E-02	9.2E-05	7.9
WALPOC	3/6/12	4.1E-04	4.3E-02	7.6E-05	6.4
WALPOC	4/13/12	7.7E-04	8.2E-02	1.4E-04	12.4
WALPOC	4/21/13	9.2E-04	9.8E-02	1.7E-04	14.9
WALPOC	5/3/13	8.4E-04	8.9E-02	1.7E-04	13.6
GS10	1/5/12	1.5E-03	1.7E-01	6.8E-04	29.6
GS10	3/6/12	2.2E-03	2.5E-01	1.2E-03	44.7
GS10	7/26/12	5.7E-04	6.2E-02	1.7E-04	10.1
GS10	4/29/13	1.2E-03	1.3E-01	4.2E-04	21.6
79102	5/14/12	3.7E-02	4.1E+00	4.1E-02	618.7

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

Sample Location	Sample Date	depleted	enriched	natural
WALPOC	9/22/11	22.53%	0.08%	77.39%
WALPOC	9/27/11	22.36%	0.07%	77.57%
WALPOC	1/3/12	20.30%	0.07%	79.63%
WALPOC	2/23/12	20.44%	0.08%	79.48%
WALPOC	3/6/12	21.57%	0.08%	78.35%
WALPOC	4/13/12	22.41%	0.06%	77.53%
WALPOC	4/21/13	22.15%	0.06%	77.79%
WALPOC	5/3/13	23.98%	0.07%	75.95%
GS10	1/5/12	47.30%	0.11%	52.59%
GS10	3/6/12	56.58%	0.13%	43.29%
GS10	7/26/12	35.59%	0.08%	64.33%
GS10	4/29/13	40.84%	0.09%	59.07%
79102	5/14/12	100.00%	0.50%	-0.50%

U Isotopic Compositions and Concentrations of Rocky Flats Water Samples Collected During 9/13/13 to 11/25/13 and Submitted to LBNL

John N. Christensen

Report date 3/20/14

Fourteen unique samples and one duplicate sample were submitted by SM Stoller to Lawrence Berkeley National Laboratory for uranium isotopic and concentration analysis. The unique samples include four from the WALPOC location, four from GS10, two from FC4EFF, two from SEEP995A, and one each from 79302 and 79502. The last two represent groundwater samples, and all others are surface water samples. These samples cover the period from June 2013 to November 2013.

METHOD:

Uranium isotopic compositions of the samples were determined at LBNL by multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS; IsoProbe model, Mfd. by Micromass) 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 ng of uranium 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 1.5 N HNO_3, centrifuged, and pipetted onto small volume Teflon columns.. Prior to sample introduction, the columns were filled with fresh TRU resin (Eichrom, Inc.), and cleaned with 0.2 M HCl and 0.3 M HF, and then conditioned with 1.5 N HNO_3. After sample loading, the columns were eluted with 1.5 N HNO_3, and then U was rinsed from the columns and collected with 0.5 N HF. 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 pg). No ^{236}U was detectible in the procedural blank solution.

Uranium isotopic compositions ($^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$) were measured on an IsoProbe 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 Daly ion counting system situated behind a wide-angle retardation potential lens. Two separate, static, and simultaneous measurement routines 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, Daly-Faraday intercalibration, and any peak-tail under mass 236 were calculated from bracketed analyses of an in-house, secular equilibrium natural uranium 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 (Aridus II manufactured by CETAC Inc.) equipped with a low uptake micro-concentric nebulizer. Typical precision for $^{235}U/^{238}U$ is ±0.05% 2σ or better; for $^{234}U/^{238}U$ and $^{236}U/^{238}U$ it is ±0.15% 2σ. $^{236}U/^{238}U$ can be measured down to and below the 10^{-7} range where precision degrades by approximately a factor of ten, with a minimum measurable ratio of $\sim 3 \times 10^{-8}$.

Using data from the IsoProbe taken through the isotopic analyses, the uranium concentrations were 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. This estimate depends on the column yield for the U separation chemistry, which is 90% or better. The given concentrations assume 100% column yield, so could be underestimated by as much as10%.

RESULTS AND DISCUSSION:

The results of the U isotopic analyses and the U concentration estimates using IsoProbe data, are provided in Table 1. The data are also presented in Figures 1 through 4. Calculated mass concentrations of ^{234}U, ^{235}U, ^{236}U, and ^{238}U based on the measured isotopic compositions and estimated U concentrations are presented in Table 2. The percentages of presumed endmembers (depleted U, enriched U, and natural U) were calculated using the Los Alamos National Laboratory (LANL) model spreadsheet and are provided in Table 3.

All analyzed samples fall within the triangle defined by natural U, the LANL-defined depleted U and enriched U endmembers (Fig. 1). Figure 2 shows a blow-up of the region of Figure 1 and compares the results of Batch #1 to Batch #2. (Batch #1 samples were collected from September 2011 through May 2013.) In Figure 2, WALPOC water samples collected on 6/4/13 and 9/13/13 have similar U isotopic compositions to previously-analyzed WALPOC samples (see report on Batch #1 samples), falling within the cluster defined by those earlier samples (grey circles). The two WALPOC samples collected on 9/14/13 and 9/16/13 fall outside this cluster toward the depleted and enriched endmembers. The four samples from GS10 fall along an extension of the trend seen in the previous GS10 samples toward the WALPOC cluster. The sample collected from FC4EFF on 11/25/13 matches nearly exactly in U isotopic composition the GS10 sample collected on the same date (Figure 2). Likewise, the FC4EFF sample of 9/30/13 is tightly bracketed in uranium isotopic composition by GS10 samples collected on 9/24/13 and 10/1/13. Samples from SEEP995A collected on 9/30/13 and 11/25/13, together with a sample collected from well 79302 on 10/29/13, appear to fall along an array sub-parallel to that formed by the WALPOC-GS10 samples but at higher fractions of the enriched endmember. A sample collected from well 79502 (near 79302) on 10/29/13 has the lowest $^{236}U/^{238}U$ ratio ($1.79 \pm 0.02 \times 10^{-6}$) of any sample we have analyzed so far, and has near-normal $^{235}U/^{238}U$ (Table 1) indicating the sample is 97% natural U (Table 3).

Combining the data for the WALPOC location from the first and second batches, a set of time-series plots can be constructed providing limited view of the changing mixture of the endmembers over the period from September 2011 through September 2013 (Figure 3). Though the limited frequency of sampling prevents firm conclusions a few observations can be made. Between 9/27/11 and 3/6/12 the fraction of enriched U changed in opposition to the fraction of depleted U, while the fraction of natural U mirrored the pattern for the fraction of depleted U. The second period of note is in the second half of 2013 where the fractions of depleted U and enriched U changed in parallel, culminating over the period 9/13/13 to 9/16/13 in a distinct, though small, rise in $^{236}U/^{238}U$ and modest increases in the fractions of enriched and depleted U.

A similar set of time series plots can be made for data from GS10 covering a similar period, although at even less sample frequency. GS10 shows an increase in $^{236}U/^{238}U$ and both the fractions of enriched and depleted U between 1/5/12 and 3/6/12; however, this is only based on two samples.

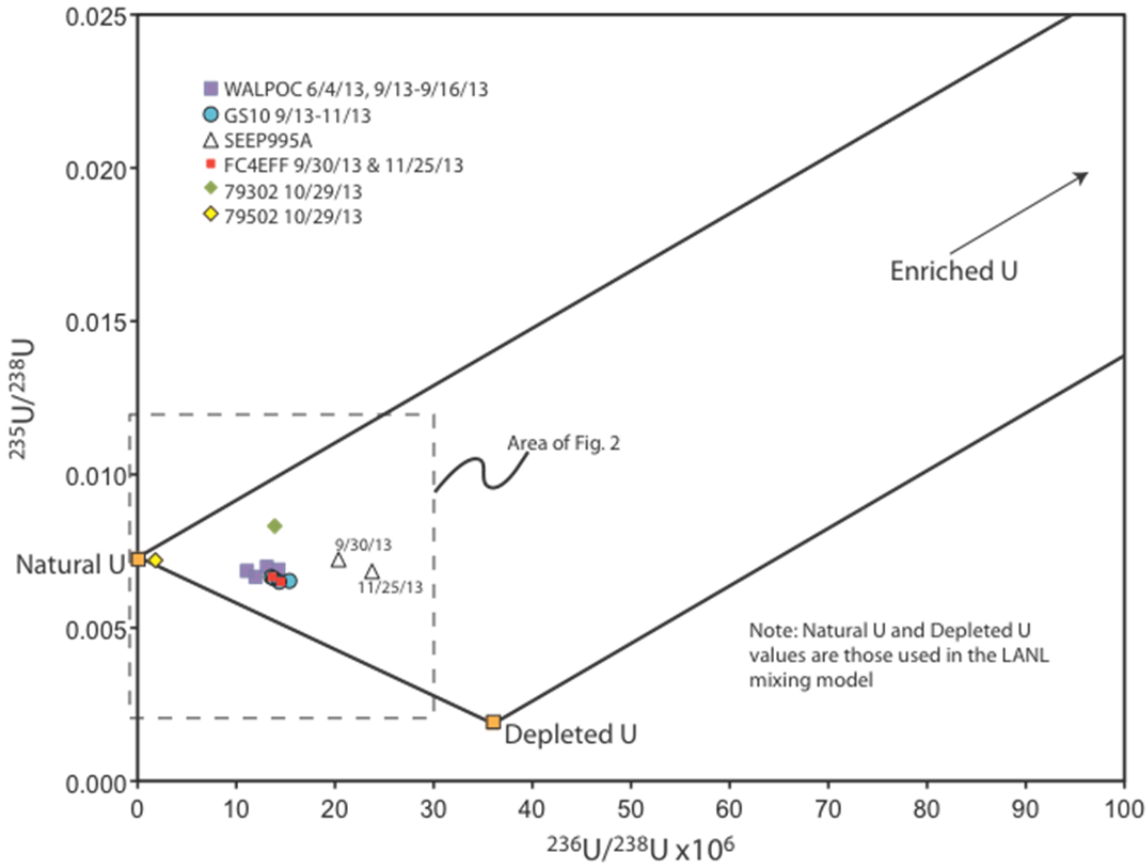
WALPOC 6/4/13, 9/13-9/16/13
GS10 9/13-11/13
SEEP995A
FC4EFF 9/30/13 & 11/25/13
79302 10/29/13
79502 10/29/13
Enriched U
Area of Fig. 2
9/30/13
11/25/13
Natural U
Depleted U
Note: Natural U and Depleted U values are those used in the LANL mixing model
0.025
0.020
0.015
0.010
0.005
0.000
235U/238U
0
10
20
30
40
50
60
70
80
90
100
236U/238U x10^6

Figure 1.

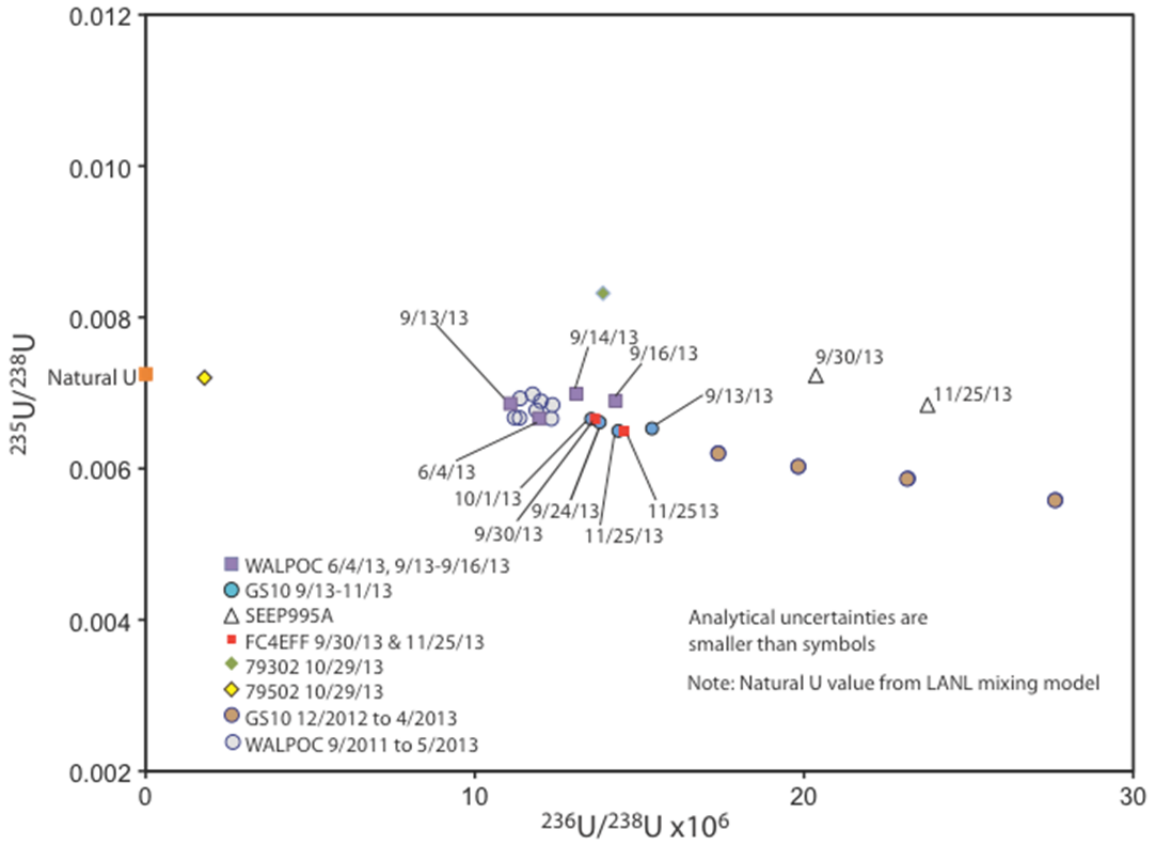
0.012
0.010
0.008
0.006
0.004
0.002
Natural U
235U/238U
0
10
20
30
236U/238U x10^6
9/13/13
9/14/13
9/16/13
9/30/13
11/25/13
9/13/13
6/4/13
10/1/13
9/24/13
9/30/13
11/25/13
11/2513
WALPOC 6/4/13, 9/13-9/16/13
GS10 9/13-11/13
SEEP995A
FC4EFF 9/30/13 & 11/25/13
79302 10/29/13
79502 10/29/13
GS10 12/2012 to 4/2013
WALPOC 9/2011 to 5/2013
Analytical uncertainties are smaller than symbols
Note: Natural U value from LANL mixing model

Figure 2.

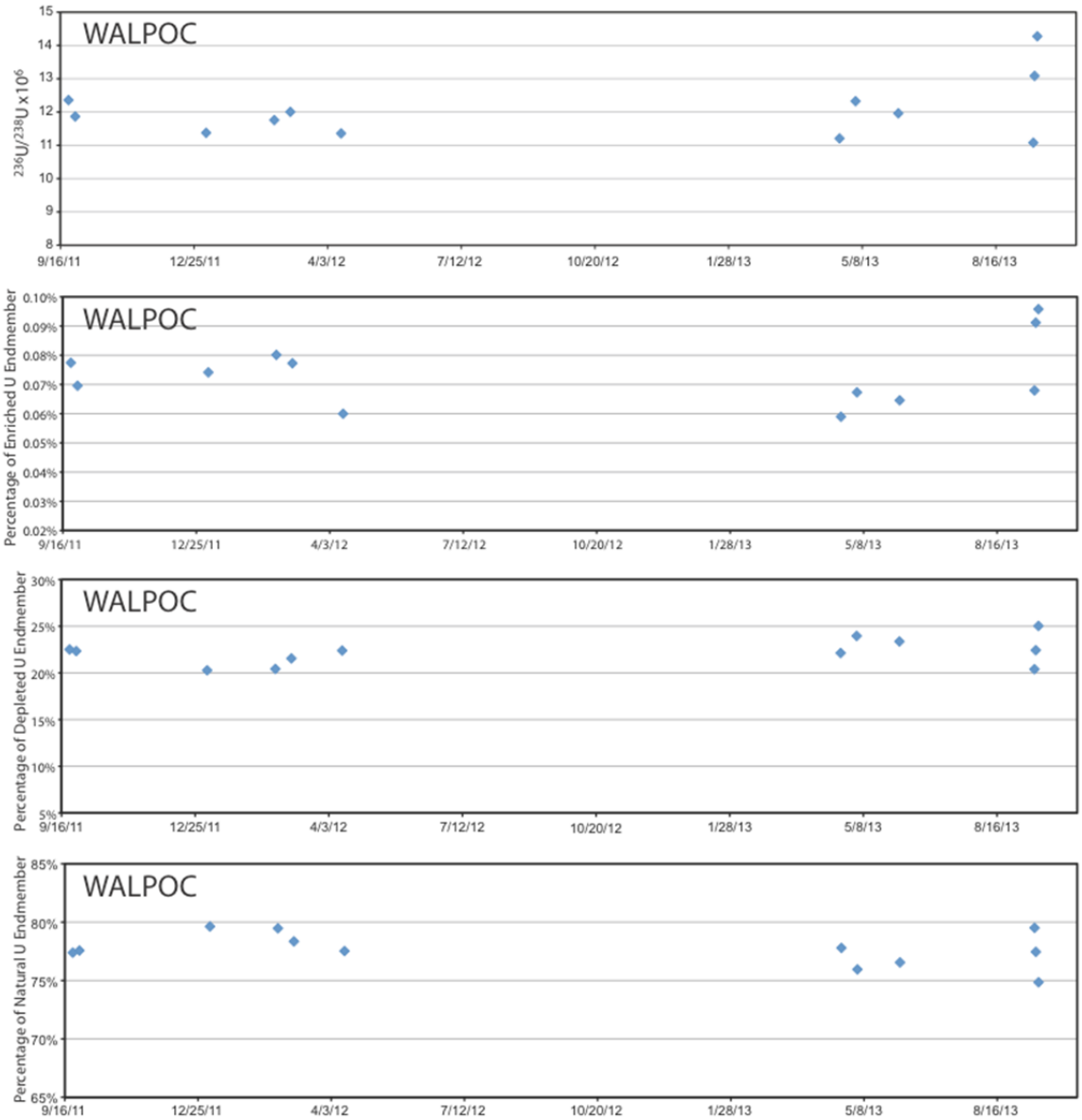
WALPOC
236U/238U x 10^6
15
14
13
12
11
10
9
8
9/16/11
12/25/11
4/3/12
7/12/12
10/20/12
1/28/13
5/8/13
8/16/13
WALPOC
Percentage of Enriched U Endmember
0.10%
0.09%
0.08%
0.07%
0.06%
0.05%
0.04%
0.03%
0.02%
WALPOC
Percentage of Depleted U Endmember
30%
25%
20%
15%
10%
5%
WALPOC
Percentage of Natural U Endmember
85%
80%
75%
70%
65%

Figure 3.

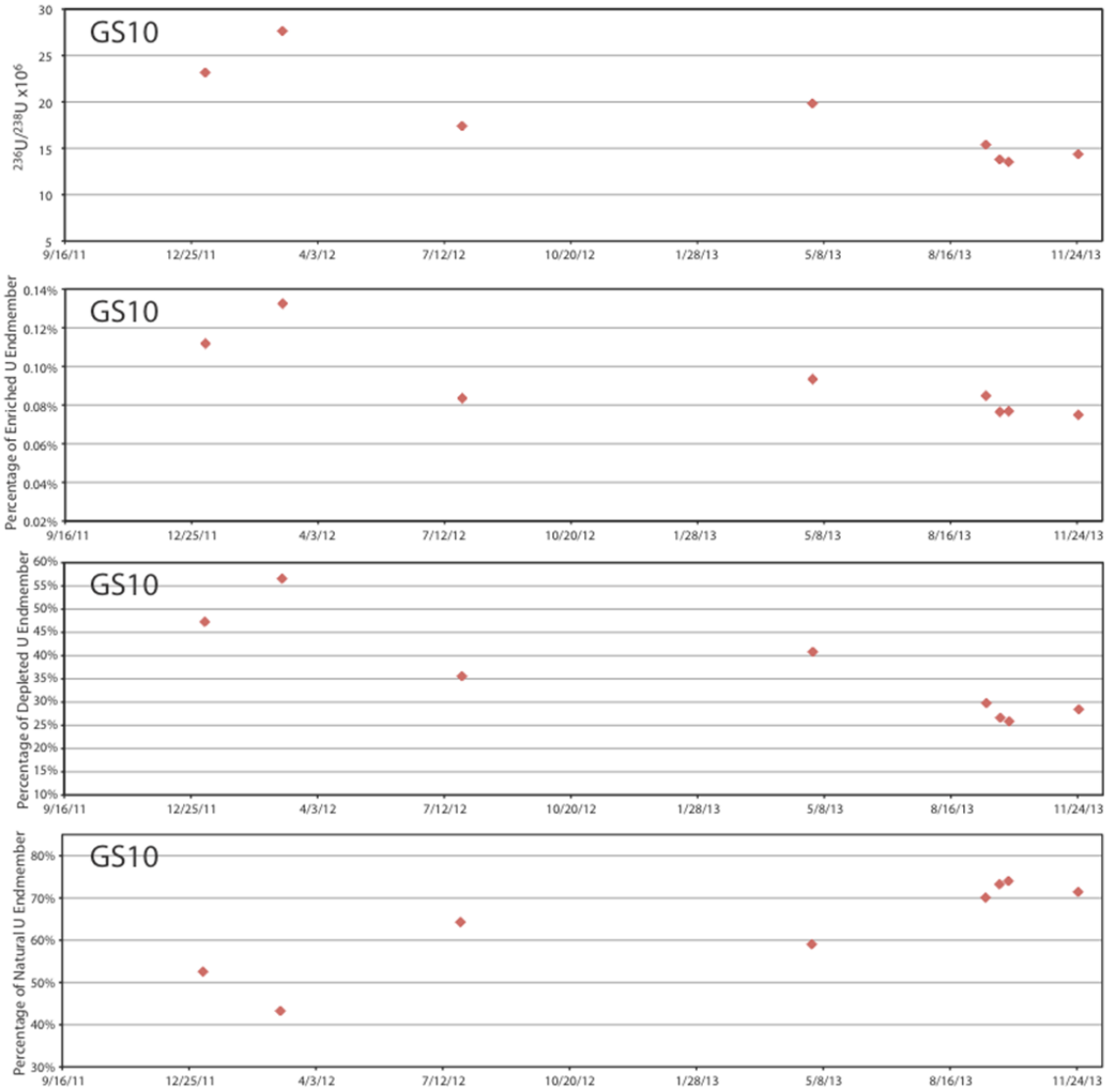
GS10
236U/238U x10^6
30
25
20
15
10
5
9/16/11
12/25/11
4/3/12
7/12/12
10/20/12
1/28/13
5/8/13
8/16/13
11/24/13
GS10
Percentage of Enriched U Endmember
0.14%
0.12%
0.10%
0.08%
0.06%
0.04%
0.02%
GS10
Percentage of Depleted U Endmember
60%
55%
50%
45%
40%
35%
30%
25%
20%
15%
10%
GS10
Percentage of Natural U Endmember
80%
70%
60%
50%
40%
30%

Figure 4.

Table 1. U isotopic compositions and U concentrations

Sample Location	Sample Date	Est. 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
FC4EFF	9/30/13	13.3	61.56	0.10	150.217	0.095	0.0066570	0.0000042	13.652	0.028
FC4EFF	11/25/13	16.5	60.15	0.12	153.953	0.09	0.0064955	0.0000038	14.531	0.027
79302	10/29/13	182.8	91.55	0.14	120.224	0.08	0.0083178	0.0000055	13.894	0.034
79502	10/29/13	11.0	97.51	0.14	138.844	0.082	0.0072023	0.0000043	1.786	0.020
SEEP995A	11/25/13	19.3	64.39	0.12	146.165	0.09	0.0068416	0.0000042	23.753	0.038
SEEP995A	9/30/13	11.2	69.29	0.13	138.311	0.08	0.0072301	0.0000042	20.36	0.032
GS10	9/13/13	5.9	58.47	0.11	153.171	0.08	0.0065287	0.0000034	15.382	0.029
GS10	9/24/13	8.1	60.17	0.11	151.253	0.09	0.0066114	0.0000039	13.794	0.035
GS10	10/1/13	11.3	61.56	0.13	150.244	0.1	0.0066558	0.0000044	13.535	0.034
GS10	11/25/13	19.4	60.18	0.10	153.885	0.085	0.0064984	0.0000036	14.360	0.024
WALPOC	6/4/13	3.6	61.69	0.15	150.062	0.22	0.0066639	0.0000098	11.962	0.032
WALPOC	9/13/13	1.7	64.50	0.10	145.823	0.078	0.0068576	0.0000037	11.079	0.029
WALPOC	9/14/13	1.9	65.78	0.09	143.126	0.12	0.0069869	0.0000059	13.085	0.030
WALPOC	9/16/13	7.0	65.17	0.11	145.031	0.075	0.0068951	0.0000036	14.275	0.030
2500	11/25/13	19.7	59.04	0.1	153.947	0.095	0.0064957	0.0000040	14.522	0.025

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

Locations 79302 and 79502 represent monitoring wells, all others are surface water locations. Location 2500 represents duplicate of sample from GS10 dated 11/25/13. All WALPOC samples are all composites, as are the GS10 samples dated 9/13/13 and 9/24/13; all other samples are grab samples.

Table 2. Concentrations of U isotopes in samples based on total U concentrations estimated from IsoProbe data

Sample Location	**Sample Date**	^{234}U µg/L	^{235}U µg/L	^{236}U µg/L	^{238}U µg/L
FC4EFF	9/30/13	8.0E-04	8.7E-02	1.8E-04	13.2
FC4EFF	11/25/13	9.7E-04	1.1E-01	2.4E-04	16.4
79302	10/29/13	1.6E-02	1.5E+00	2.5E-03	181.3
79502	10/29/13	1.0E-03	7.7E-02	1.9E-05	10.9
Seep 995a	11/25/13	1.2E-03	1.3E-01	4.5E-04	19.2
Seep 995a	9/30/13	7.6E-04	8.0E-02	2.3E-04	11.2
GS10	9/13/13	3.4E-04	3.8E-02	9.0E-05	5.9
GS10	9/24/13	4.8E-04	5.3E-02	1.1E-04	8.0
GS10	10/1/13	6.8E-04	7.4E-02	1.5E-04	11.3
GS10	11/25/13	1.1E-03	1.2E-01	2.7E-04	19.2
WALPOC	6/4/13	2.2E-04	2.3E-02	4.2E-05	3.6
WALPOC	9/13/13	1.1E-04	1.2E-02	1.9E-05	1.7
WALPOC	9/14/13	1.2E-04	1.3E-02	2.4E-05	1.9
WALPOC	9/16/13	4.4E-04	4.7E-02	9.8E-05	6.9
2500	11/25/13	1.1E-03	1.3E-01	2.8E-04	19.6

Note: Locations 79302 and 79502 represent monitoring wells, all others are surface water locations. Location 2500 represents duplicate of sample from GS10 dated 11/25/13. All WALPOC samples are all composites, as are the GS10 samples dated 9/13/13 and 9/24/13; all other samples are grab samples.

Table 3. Percentages of endmembers calculated using the LANL model

Sample Location	Sample Date	Depleted	Enriched	Natural
FC4EFF	9/30/13	26.06%	0.08%	73.86%
FC4EFF	11/25/13	28.75%	0.08%	71.17%
79302	10/29/13	12.69%	0.17%	87.14%
79502	10/29/13	3.18%	0.01%	96.81%
SEEP995A	11/25/13	40.16%	0.17%	59.67%
SEEP995A	9/30/13	31.70%	0.16%	68.14%
GS10	9/13/13	29.80%	0.08%	70.12%
GS10	9/24/13	26.65%	0.08%	73.27%
GS10	10/1/13	25.89%	0.08%	74.04%
GS10	11/25/13	28.47%	0.07%	71.46%
WALPOC	6/4/13	23.39%	0.06%	76.55%
WALPOC	9/13/13	20.42%	0.07%	79.52%
WALPOC	9/14/13	22.45%	0.09%	77.46%
WALPOC	9/16/13	25.05%	0.10%	74.85%
2500	11/25/13	28.74%	0.08%	71.19%

Note: Locations 79302 and 79502 represent monitoring wells, all others are surface water locations. Location 2500 represents duplicate of sample from GS10 dated 11/25/13. All WALPOC samples are all composites, as are the GS10 samples dated 9/13/13 and 9/24/13; all other samples are grab samples.