

**U Isotopic Compositions and Concentrations of Rocky Flats Water Samples
Collected Over the Period 4/8/14 to 1/6/15 and Submitted to LBNL**

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Seven surface water samples were submitted by Stoller Newport News Nuclear to Lawrence Berkeley National Laboratory for uranium (U) isotopic analysis. The samples include three composite samples from the WALPOC location; three composite samples from GS10; and one composite sample from the SW093 location. These samples were collected during the period from April 2014 through early January 2015 (see Table 1 for specific dates).

METHODS:

U isotopic compositions of the samples were determined at LBNL by multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS; IsoProbe model, manufactured 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 U and transferred to new Teflon vials and dried down. After drying down, the samples were taken up in 8 N HNO₃ and re-dried. The samples were then taken up in 1.5 N HNO₃, centrifuged, and pipetted onto small-volume Teflon columns. Prior to sample introduction, the columns were filled with fresh UTEVA resin (Eichrom, Inc.) (prior to use, this resin is cleaned by repeated suspension, settling and decanting of supernate using de-ionized water), and cleaned on the column with 0.05 M HCl, and then conditioned with 3 N HNO₃. (Prior to use, the resin is cleaned by repeated suspension, settling and decanting of supernate using de-ionized water.) After sample loading, the columns were eluted with 3 N HNO₃ 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 pg). No ^{236}U was detectable in the procedural blank solution.

U isotopic compositions ($^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$) 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 $^{235}\text{U}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ and a second for $^{236}\text{U}/^{238}\text{U}$. Corrections for mass fractionation, Daly-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 $^{238}\text{U}/^{235}\text{U}$ 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 $^{235}\text{U}/^{238}\text{U}$ is $\pm 0.05\%$ 2σ or better, and for $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ it is $\pm 0.15\%$ 2σ . $^{236}\text{U}/^{238}\text{U}$ 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 $\sim 5 \times 10^{-8}$.

Using data from the IsoProbe taken through the isotopic analyses, the U concentration for sample WALPOC (10/23/14-1/6/15) 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. This estimate depends on the column yield for the U separation chemistry, which is better than 90%. The given

concentration assumes 100% column yield, so it could be underestimated by as much as 10%.

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 Figure 3 and for GS10 samples in Figure 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 20% of each other (most within 15%).

Results for all seven analyzed samples fall within the triangle defined by natural U, the LANL-defined depleted U, and enriched U end-members (Fig. 1, shown at same scale as in previous reports). Because the current set of samples fall closely together in Figure 1, a blow-up is shown in Figure 2 comparing the current set of surface water samples to previous analyses of WALPOC samples (9/22/11 to 4/15/14; see LBNL reports dated 9/16/13, 3/20/14, and 6/16/14) and GS10 samples (1/5/12 to 11/25/13; see LBNL reports dated 9/16/13 and 3/20/14).

WALPOC composite samples collected 5/14/14-5/21/14, 8/12/14-10/23/14, and 10/23/14-1/6/15 fall on either side of the tight cluster defined by previously analyzed WALPOC samples (sampling dates range from 9/22/11 to 9/13/14) (Figures 2 and 5). WALPOC samples collected 8/12/14-10/23/14 and 10/23/14-1/6/15 are similar to the WALPOC sample collected on 2/13/14 and have relatively low $^{236}\text{U}/^{238}\text{U}$, while the WALPOC sample collected 5/14/14-5/21/14 has the third highest $^{236}\text{U}/^{238}\text{U}$ of the WALPOC samples, exceeded only by WALPOC samples collected on 9/16/13 and 11/23/13.

The three GS10 composite samples analyzed for this report fall in the upper portion of the array defined by previous GS10 samples (Figures 1 and 2). The composite sample collected 10/2/14-11/19/14 from SW093 has the second highest (second most enriched) $^{235}\text{U}/^{238}\text{U}$ with a ratio of 0.007479 ± 8 ; the highest $^{235}\text{U}/^{238}\text{U}$ ratio (0.008418 ± 6) is for a sample from well 79302 (located immediately north of the former Solar Evaporation Ponds) collected on 10/29/13.

The long-term (September 2011 to January 2015) changes in the U isotopic composition and concentration in WALPOC samples are shown as a set of time-series plots in Figure 3. The three most recent samples analyzed (this report) nearly cover the whole range in U isotopic composition of previously analyzed samples. The 5/14/14-5/21/14 composite sample has a higher $^{236}\text{U}/^{238}\text{U}$ than samples collected from January – April 2014, but not quite as high as samples collected in fall 2013.

In Figure 4, the long-term changes in U isotopic composition and concentration for GS10 samples, including three samples from this report, are shown as a time-series. The overall trend, with reversals, is toward lower $^{236}\text{U}/^{238}\text{U}$, lower percentages of the depleted U and enriched U endmembers, and a higher percentage of natural U. Over the long term shown, U concentration has gone up and down by 10's of ppb, but overall may have a downward trend.

In Figure 5, U isotopic data produced at LBNL for samples collected at the WALPOC and GS10 locations, along with other geographically related samples, are plotted. This figure focuses both on U isotopic changes with time as well as on the geographic locations of the samples. GS10 samples fall along an array indicating variable mixing with natural uranium (e.g., dashed lines), with the proportion of natural U, in general, increasing with time. GS10 samples collected on 1/5/12, 3/6/12, 7/26/12, and 4/29/13 (labeled 1 through 4 on Figure 5) appear to have an anthropogenic endmember (A off scale in Figure 5, cf. Figure 1) with a lower $^{236}\text{U}/^{238}\text{U}$ than the anthropogenic endmember (B off scale in Figure 5, cf. Figure 1) for GS10 samples collected on 9/13/13, 9/24/13, and 10/1/13. Later GS10 samples (11/25/13, 4/8/14-4/22/14, 7/10/14-7/30/14, and 10/2/14-10/23/14) indicate an anthropogenic endmember intermediate in $^{236}\text{U}/^{238}\text{U}$ but trending back to the anthropogenic endmember (A) for the earlier GS10 samples (1/5/12, 3/6/12,

7/26/12, and 4/29/13). These anthropogenic endmembers (A and B) are shown in Figure 1 sitting on the line joining the model depleted U composition and the model enriched U composition, but could lie further along the dashed mixing lines with natural U.

Samples collected along South Walnut Creek downstream of GS10 (B5INFLOW, B5 Pond, and GS08) are consistent with the addition of natural U to GS10 compositions (i.e., those samples lie along extensions of mixing lines that include GS10 and natural U). In the case of samples collected along North Walnut Creek, the farthest upstream sample, SW093, has a distinct signature of enriched U (as noted above, it has the second highest $^{235}\text{U}/^{238}\text{U}$ ratio of the surface water samples, and at 0.17% the second highest percentage of the model enriched U component). Samples collected downstream from SW093 (GS11 and GS12 composite samples on 4/2/14-4/16/14 and GS11 and A4 Pond samples collected on 2/13/14) indicate that between the locations of GS11 and SW093 there is an addition of anthropogenic U with a lower fraction of enriched U rather than simple addition of natural U.

Samples at the WALPOC location represent mixtures of water coming from South and North Walnut Creeks that is reflected in the U isotopic compositions of WALPOC samples. For example, the WALPOC sample collected on 2/13/14 lies within the mixing triangle (shown in pink shading in Figure 5) defined by natural U, sample GS11 collected on 2/13/14, and sample GS08 collected on 2/13/14). The grey-shaded triangle generalizes this relationship to include all measured WALPOC U isotopic compositions, and shows how variability in both the proportions of U from South Walnut Creek versus North Walnut Creek and in the U isotopic compositions of their outflow (represented by GS08 and GS11) can explain the observed U isotopic variability of WALPOC samples.

Reference

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

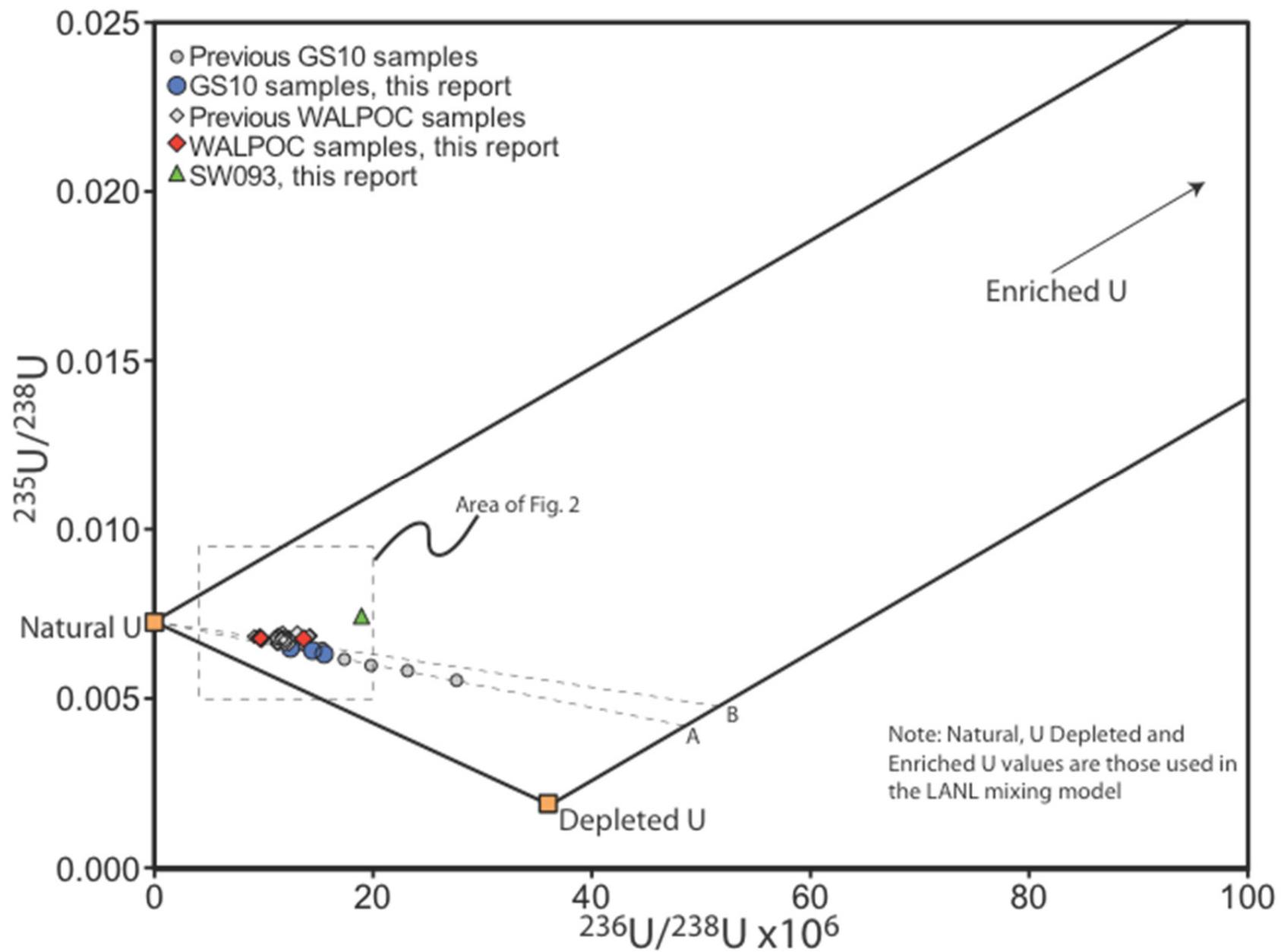


Figure 1.

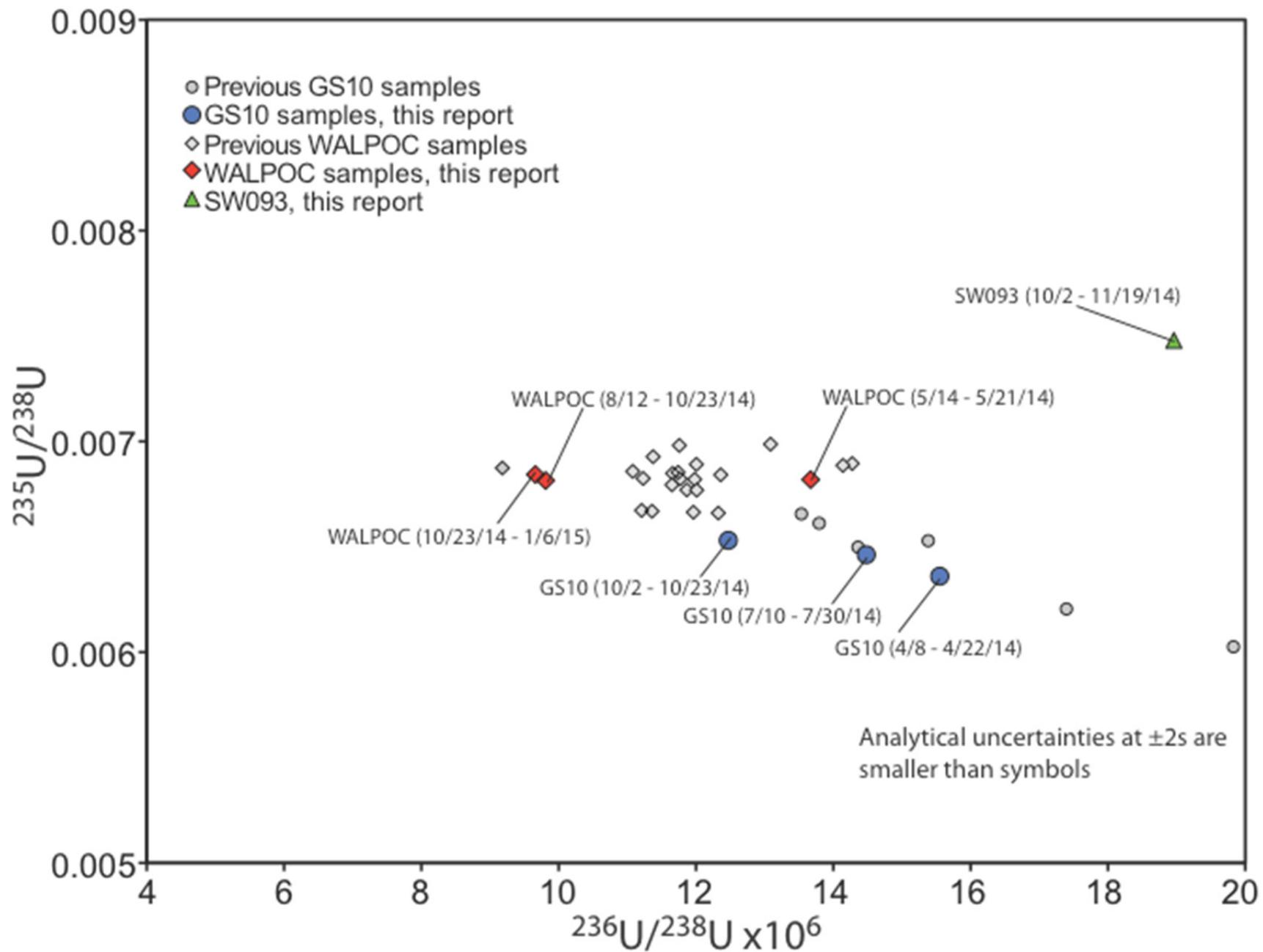


Figure 2.

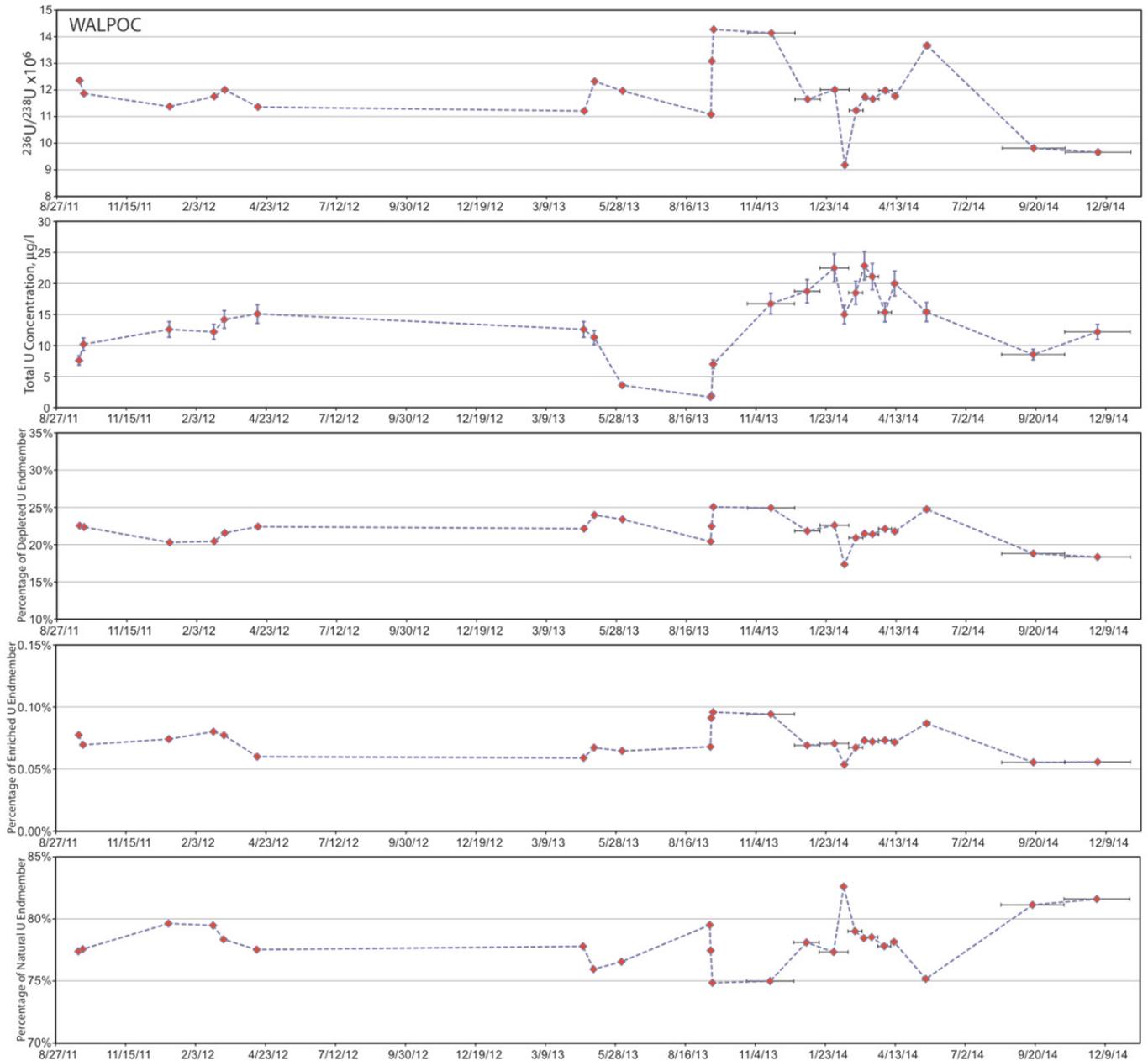


Figure 3. Note: Time spans of composite samples are represented by horizontal bars, in some cases smaller than the data symbols.

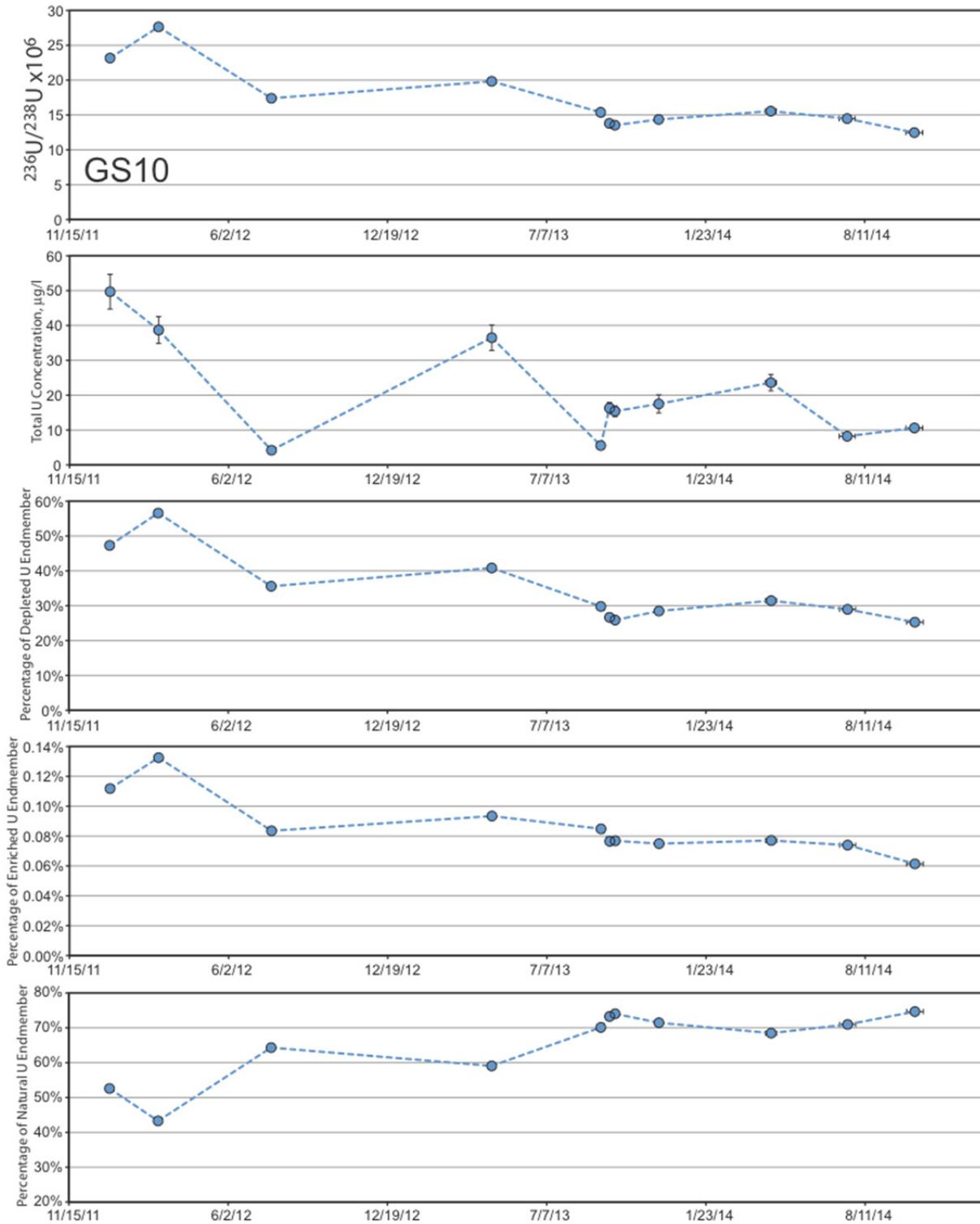


Figure 4. Note: Time spans of composite samples are represented by horizontal bars, in some cases smaller than the data symbols.

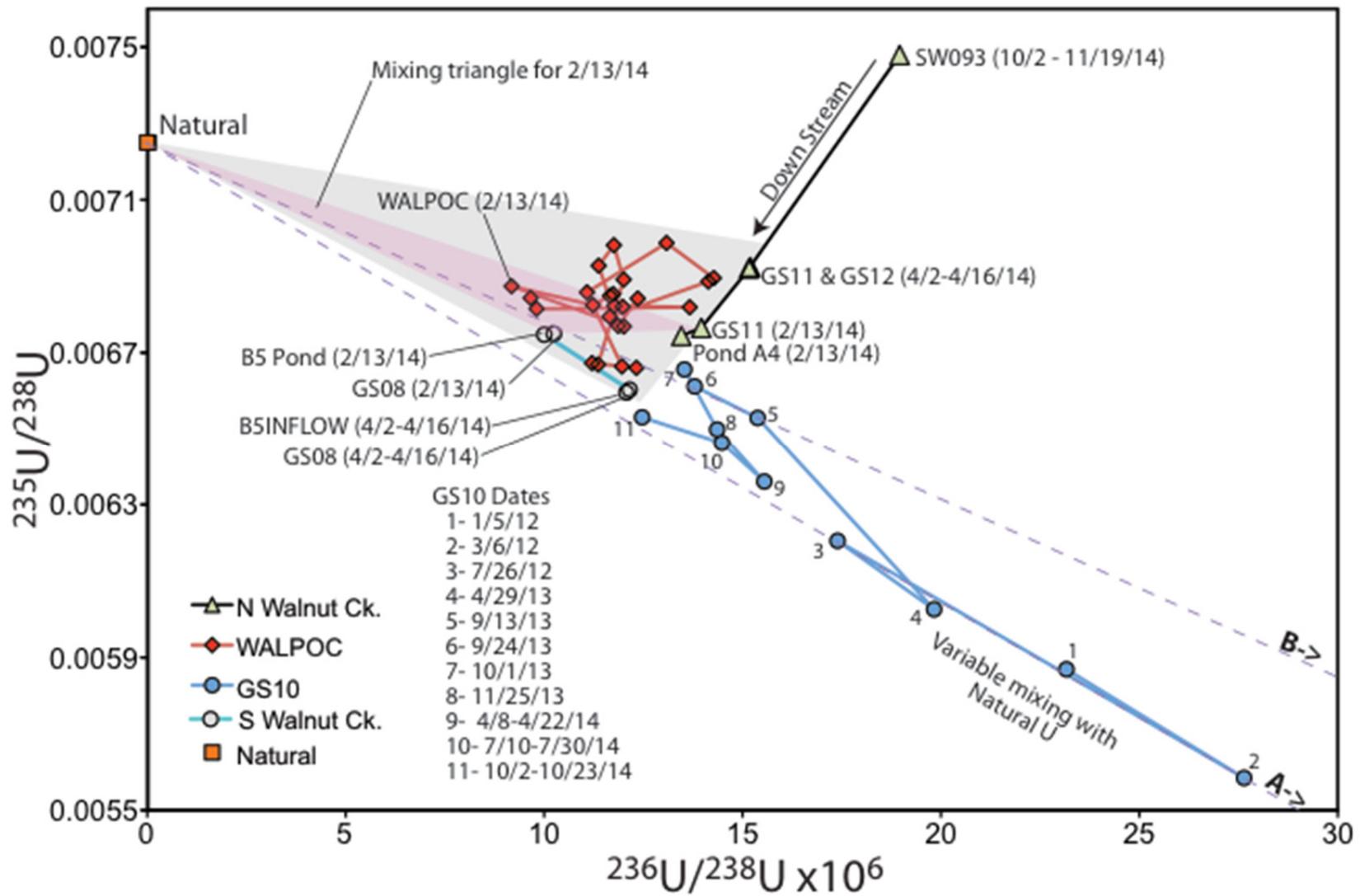


Fig. 5

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
GS10	4/8/14-4/22/14	Comp.	23.6	58.54	0.11	157.225	0.230	0.0063603	0.0000093	15.55	0.10
GS10	7/10/14-7/30/14	Comp.	8.2	59.72	0.10	154.741	0.197	0.0064624	0.0000082	14.48	0.10
GS10	10/2/14-10/23/14	Comp.	10.6	61.48	0.12	153.130	0.088	0.0065304	0.0000038	12.47	0.10
WALPOC	5/14/14-5/21/14	Comp.	15.4	64.39	0.10	146.655	0.109	0.0068187	0.0000051	13.67	0.10
WALPOC	8/12/14-10/23/14	Comp.	8.6	65.64	0.09	146.747	0.111	0.0068144	0.0000052	9.81	0.08
WALPOC	10/23/14-1/6/15	Comp.	12.2*	65.50	0.09	146.136	0.092	0.0068429	0.0000043	9.66	0.09
SW093	10/2/14-11/19/14	Comp.	4.7	72.47	0.1	133.706	0.150	0.0074791	0.0000084	18.96	0.10

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

‡Concentrations from Contract Lab, except for *

*Estimated by IsoProbe beam intensity data.

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
GS10	4/8/14-4/22/14	1.3E-03	1.5E-01	3.6E-04	23.4
GS10	7/10/14-7/30/14	4.8E-04	5.2E-02	1.2E-04	8.2
GS10	10/2/14-10/23/14	6.4E-04	6.8E-02	1.3E-04	10.5
WALPOC	5/14/14-5/21/14	9.7E-04	1.0E-01	2.1E-04	15.3
WALPOC	8/12/14-10/23/14	5.5E-04	5.7E-02	8.3E-05	8.5
WALPOC	10/23/14-1/6/15	7.8E-04	8.2E-02	1.2E-04	12.1
SW093	10/2/14-11/19/14	3.3E-04	3.4E-02	8.8E-05	4.7

Table 3. Percentages of endmembers calculated using the LANL model

Sample Location	Sample Date(s)	Depleted	Enriched	Natural
GS10	4/8/14-4/22/14	31.4%	0.08%	68.5%
GS10	7/10/14-7/30/14	28.9%	0.07%	71.0%
GS10	10/2/14-10/23/14	25.3%	0.06%	74.7%
WALPOC	5/14/14-5/21/14	24.7%	0.09%	75.2%
WALPOC	8/12/14-10/23/14	18.8%	0.06%	81.1%
WALPOC	10/23/14-1/6/15	18.3%	0.06%	81.6%
SW093	10/2/14-11/19/14	27.5%	0.17%	72.4%

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

Sample Location	Sample Date(s)	Contract Lab	LBNL	Percent Difference
GS10	4/8/14-4/22/14	23.6	25.4	+8%
GS10	7/10/14-7/30/14	8.2	8.9	+8%
GS10	10/2/14-10/23/14	10.6	9.4	-11%
WALPOC	5/14/14-5/21/14	15.4	16.8	+9%
WALPOC	8/12/14-10/23/14	8.6	9.7	+14%
WALPOC	10/23/14-1/6/15	n.d.	12.2	-----
SW093	10/2/14-11/19/14	4.7	5.6	+19%