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**Variation in Uranium Isotopic Ratios $^{238}\text{U}/^{235}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ and
 $^{236}\text{U}/^{238}\text{U}$
in Water Samples Collected from Private Wells in the Española
Basin, Santa Fe, New Mexico**

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I. Executive Summary

This report presents uranium concentration and variation in uranium isotopic ratios $^{238}\text{U}/^{235}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ in water samples collected from private wells in the Española basin in New Mexico. The document focuses specifically on analyzing variations in the uranium isotopic composition of the different water samples. The data presented in this report were obtained from water samples collected during the fall of 2012. A list of the different sampling locations as identified by their GPS coordinates is presented in Table 1 and represented on a map shown in Figure 1. Water temperature, conductivity, pH, and redox conditions (ORP) were also measured at the time of sampling and are also presented in Table 1.

The pH of the samples ranged between 7.10 and 8.49, the temperature between 11.30 and 16.58 °C, and the ORP between -182 and 202 mV. The conductivity of the samples was between 454 $\mu\text{S}\cdot\text{cm}^{-1}$ and 1066 $\mu\text{S}\cdot\text{cm}^{-1}$. The concentration of uranium in the samples varied widely and ranged between 11.5 and 776 $\mu\text{g}/\text{L}$. Uranium isotopic ratios conducted by Thermal Ionization Mass Spectrometry (TIMS) showed natural $^{238}\text{U}/^{235}\text{U}$ within analytical uncertainty. The water samples showed some variations in the isotopic ratios of $^{234}\text{U}/^{238}\text{U}$, varying from atom ratios of 54.9×10^{-6} to 226×10^{-6} (activity ratios of 1.00 to 4.11), and indicating enrichment of ^{234}U in many of the water samples. These isotopic ratios are within the range observed in natural water. Such enrichments in ^{234}U in natural waters are common and typically attributed to natural processes. There was no detectable ^{236}U in any of the samples analyzed.

II. Background

Uranium has three naturally occurring isotopes: ^{234}U , ^{235}U and ^{238}U . Their half-lives are 2.45×10^5 years for ^{234}U , 7.04×10^8 for ^{235}U , and 4.47×10^9 years for ^{238}U . Their natural isotope abundance ratios, or atom ratios, are approximately 0.000055:0.00725:1 for ^{234}U : ^{235}U : ^{238}U . The isotopic ratio $^{238}\text{U}/^{235}\text{U}$ in nature is relatively constant and the value has long been accepted to be 137.88 [1] based on analysis of uranium isotopic composition in magmatic rocks. This ratio has been revised recently based on the analysis of a large number of U-bearing accessory minerals that are used for U-Pb geochronology and was assigned a value of 137.818 ± 0.045 [2]. Very small variations in the isotopic ratios exist among samples and are due to natural isotope fractionation. If secular equilibrium is preserved, the isotopic ratio of $^{234}\text{U}/^{238}\text{U}$ is approximately 55.0×10^{-6} , equivalent to an activity ratio of 1. However, in natural samples this ratio varies considerably. The main mechanisms that affect the $^{234}\text{U}/^{238}\text{U}$ ratio are direct ejection of ^{234}U from the crystal lattice during alpha decay of its parent (^{234}Th), preferential leaching of ^{234}U from crystal lattice damaged as a result of alpha decay, and preferential oxidation of ^{234}U . The activity ratio $^{234}\text{U}/^{238}\text{U}$ in water varies from 0.5 to >40 [3], while in soil typically ranges from 0.5 to 1.2 [3]. ^{236}U is formed by neutron capture of ^{235}U in a nuclear reactor and its presence is generally attributable to anthropogenic uranium. The ratio of $^{236}\text{U}/^{238}\text{U}$ can be used to detect nuclear activities or assign an anthropogenic origin to natural samples.

Los Alamos National Laboratory (LANL) was asked for assistance in determining the isotopic composition of uranium present in private wells in the Española basin in New Mexico. LANL assisted with a sampling campaign in the fall of 2012 and collected 13 samples from different private wells. Uranium isotopic characterization was performed using TIMS analysis and the results obtained were compared to the standard isotopic ratios available in the literature.

III. Water sampling and processing

1. Water sampling procedure

A total of 13 water samples were obtained from different private wells. Each well was identified by using global positioning system (GPS) coordinates. The sampling team collected the groundwater samples in pre-washed 150 ml low density polyethylene (LDPE) bottles (Nalgene) acid washed and rinsed in the laboratory. Controls from the laboratory were also prepared and transported to the field and handled according to the same procedure applied to the field samples. The field sampling procedure consisted of collecting the ground water from a line of a water pump that is located before any water treatment devices. The pump was allowed to run until the temperature readings were stable before the samples were collected. The sampling team recorded water parameters such as temperature, pH, conductivity and ORP *in situ* using a multi-probe reading device. All water samples collected for uranium isotope analysis were filtered in the field using a 0.45 μm syringe filters. The bottles filled with filtered water were stored on ice until they were transferred to a refrigerator and then stored at 4°C until analyzed.

2. Uranium Purification

An aliquot was taken from each of the original sample containers to yield approximately 200 ng of U. The aliquots were acidified by approximately 2 mL concentrated nitric acid (Optima grade, Fisher Scientific) to digest any organic material that might be present in the sample. The acidified samples were brought to dryness on a hotplate and using heat lamp. The sample residue was evaluated to determine if more digestion is required. Most of the samples analyzed during this study were clean and did not require any further digestion.

To the dried samples were added approximately 0.7 ng of ^{233}U spike (tracer). The spiked samples were re-dissolved in 3M HCl and then 0.5 ml HClO_4 and 5 drops saturated H_3BO_3 were added to each sample. The samples were left to equilibrate overnight at room temperature. Perchloric acid was used to equilibrate the spike and sample and to oxidize all uranium to U(VI). Boric acid was used to remove insoluble fluorides. The equilibrated samples were fumed in hood until dry and perchloric acid fumes were gone. The residues were then dissolved in 8.0 M HCl and dried on a hot plate. This step converts the uranium complex to the chloride form for anion exchange purification. The chloride U form was purified using three separate purification columns (Bio Rad MP-1M anion exchange resin). The first column separates plutonium and thorium from uranium; the second and third columns further remove sample matrix and purify the uranium. Following the third (last) column clean up, samples were refluxed overnight in 7.5 M HNO_3 . The samples were inspected for suitability for TIMS analysis and loaded on a pre-

cleaned and conditioned rhenium filament using dilute nitric acid. The filament was loaded into the TIMS instrument for analysis.

IV. Results and Discussion

Thirteen wells were sampled and their water samples processed for total uranium and uranium isotopic analysis. In addition, three wells were randomly selected for duplicate sampling. In addition to these 16 samples, a control sample provided by the C-NR laboratory was taken to the field and was processed using the same procedure applied for the well samples. The list of all samples collected along with the water parameters measured in the field are presented in Table 1 and sample locations are shown in Figure 1.

All water samples exhibited minor variations in pH, conductivity, temperature, and redox conditions. The pH values varied from 7.10 to 8.49 and the water samples conductivity from 454 to 1066 $\mu\text{S}/\text{cm}$. The redox measurements were also consistent among all samples and were all oxidizing except UAS-ST-101112-15, which was reducing with an ORP reading of -182 mV.

Uranium concentrations, shown in Table 2, are quite variable, ranging from 11.5 to 776 $\mu\text{g}/\text{L}$. Even the lowest of these concentrations are still quite high compared to typical groundwater, which generally have uranium concentrations between 1 and 5 $\mu\text{g}/\text{L}$. Values >100 $\mu\text{g}/\text{L}$ are extremely elevated. Such high concentrations of uranium are likely due to high concentrations of uranium in the aquifer rocks combined with favorable water chemistry for solubilizing uranium. It is noteworthy that one of the duplicates run in this study (old Santa Fe Trail) shows a large variation in the uranium concentration with values of 11.5 and 20.2, but consistent isotope ratios. The differences in uranium concentration are too large to be analytical and more likely suggest some real variation generated during well pumping.

The atom and corresponding activity ratios for $^{238}\text{U}/^{235}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ for all samples are presented in Table 2. There was no detectable ^{236}U in any of the samples analyzed so $^{236}\text{U}/^{238}\text{U}$ ratios could not be calculated. Within analytical uncertainty, $^{238}\text{U}/^{235}\text{U}$ atom ratios are equivalent to the natural value of 137.818 ± 0.045 (Hiess, et al., 2012), which is equivalent to an activity ratio of approximately 21.70. The water samples showed variations in the $^{234}\text{U}/^{238}\text{U}$ atom ratios from 54.9×10^{-6} to 226×10^{-6} , which correspond to activity ratios from 1.00 to 4.11. These values indicate natural enrichment in ^{234}U , and are within the range commonly observed in natural waters [3].

V. Conclusions

Uranium concentrations vary between 11.5 and 776 $\mu\text{g}/\text{L}$ for the thirteen samples collected from private wells from the Española basin and all but four sample locations exceed the MCL of 30 $\mu\text{g}/\text{L}$. Isotopic ratios of $^{238}\text{U}/^{235}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ are all within the range expected for natural environmental waters. There was no detectable ^{236}U in any of the samples analyzed.

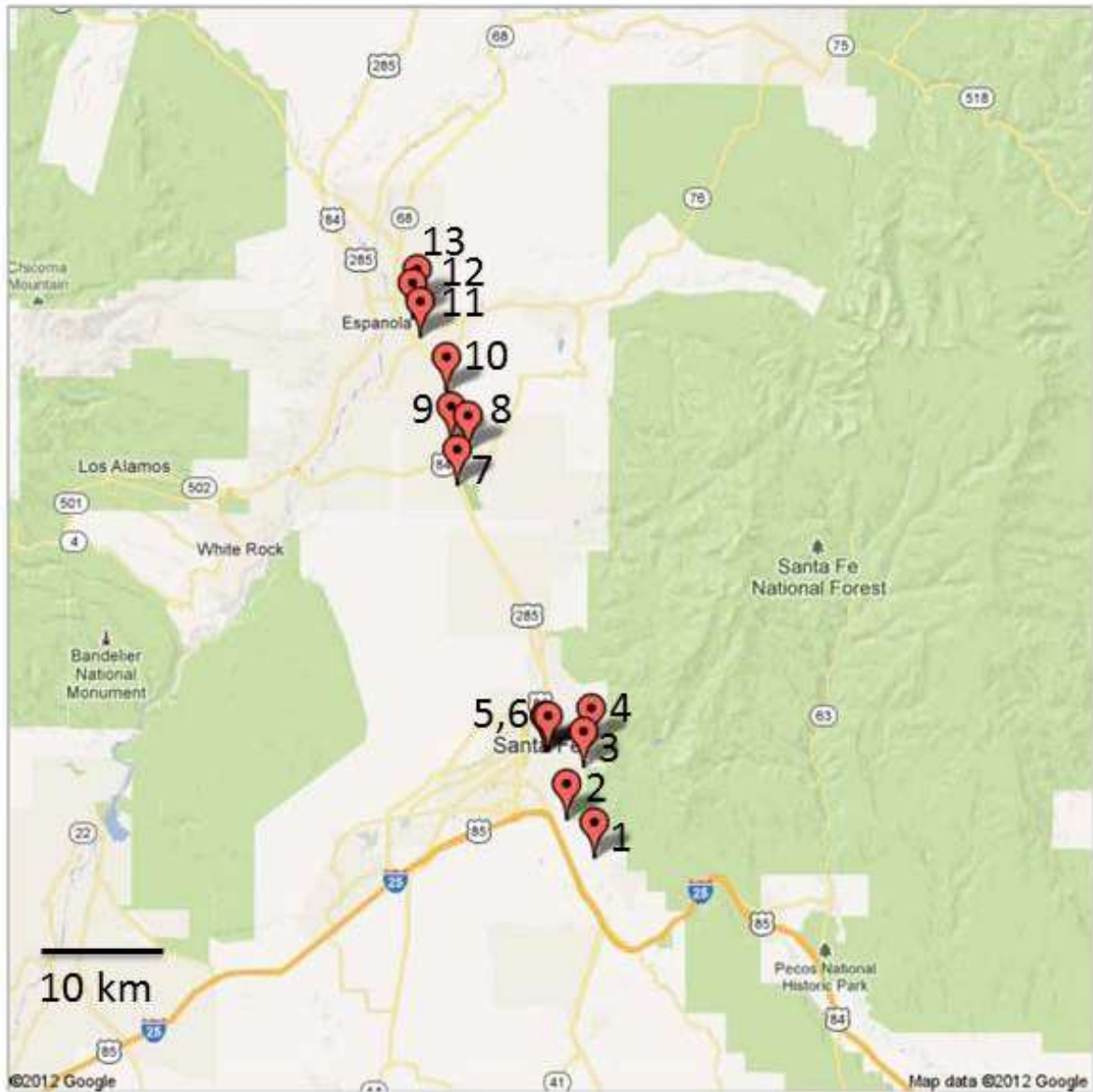


Figure 1. Map showing the location of the well samples obtained during sampling campaign performed in the fall of 2012.

Table 1. Location of wells sampled and initial water parameters.

Map #	Sample ID	Location ID	GPS coordinates	Elevation (ft amsl)	Temp in °C	pH	Conductivity in $\mu\text{S/cm}$	ORP in mV
1	UAS-ST-101112-1	Old SF Trail	35° 37.892 N 105° 54.734 W	7318	15.72	7.49	919	202
1	UAS-ST-101112-2	Old SF Trail (duplicate)						
2	UAS-ST-101112-3	Old SF Trail	35° 36.190 N 105° 53.254 W	7570	13.25	7.37	1005	62
3	UAS-ST-101112-4	Acequia Madre	35° 40.846 N 105° 55.864 W	7100	13.68	7.88	454	97
4	UAS-ST-101112-5	Cam. Cruz Blanca	35° 40.159 N 105° 53.763 W	7663	15.40	7.52	769	157
4	UAS-ST-101112-6	Cam. Cruz Blanca (duplicate)						
5	UAS-ST-101112-7	Upper Canyon Rd.	35° 41.186 N 105° 53.454	7437	11.30	7.31	828	200
6	UAS-ST-101112-8	Tesuque	31° 47.195 N 105° 54.140 W	7272	15.91	7.82	654	166
7	UAS-ST-101112-9	Pojoaque	35° 52.355 N 106° 00.586 W	5957	12.59	7.58	637	115
8	UAS-ST-101112-10	Nambe (Bouquet Lane)	35° 54.278 N 106° 00.941W	5865	14.48	7.53	1066	124
9	UAS-ST-101112-11	Nambé (Sarma Lane)	35° 53.891 N 105° 59.981W	5910	15.48	8.48	495	81
9	UAS-ST-101112-12	Nambé (Sarma Lane) (duplicate)						
10	UAS-ST-101112-13	Santa Cruz	35° 59.676 N 106° 02.949 W	5636	16.58	7.27	660	124
11	UAS-ST-101112-14	Española	36°00.193N 106°.02.745 W	5658	15.34	7.18	716	170
12	UAS-ST-101112-15	La Mesilla	35° 58.816 N 106° 02.590 W	5720	15.01	7.10	938	142
13	UAS-ST-101112-16	Arroyo Seco	35° 56.394 N 106° 01.139	5903	16.40	8.49	561	-182

Table 2. Uranium isotope ratios and total uranium concentrations for well water samples, duplicates, and controls (errors are 2 standard errors of the mean).

Sample ID	Sample Name	[U] μg/L	(+/-) %	²³⁸ U/ ²³⁵ U atom ratio	(+/-) %	²³⁸ U/ ²³⁵ U activity ratio	²³⁴ U/ ²³⁸ U atom ratio (×10 ⁻⁶)	(+/-) %	²³⁴ U/ ²³⁸ U activity ratio	²³⁶ U/ ²³⁵ U
UAS-ST-101112-1	Old SF Trail 1	11.5	0.6	137.93	0.2	21.72	225.5	0.2	4.10	BDL*
UAS-ST-101112-2	Old SF Trail 1 <i>duplicate</i>	20.2	0.6	137.86	0.2	21.71	226.0	0.2	4.11	BDL
UAS-ST-101112-3	Old SF Trail 2	35.7	0.7	138.04	0.2	21.73	118.9	0.3	2.16	BDL
UAS-ST-101112-4	Acequia Madre	12.4	0.6	137.90	0.1	21.71	118.4	0.2	2.15	BDL
UAS-ST-101112-5	Cam. Cruz Blanca	117	0.6	137.83	0.2	21.70	145.7	0.2	2.65	BDL
UAS-ST-101112-6	Cam. Cruz Blanca <i>duplicate</i>	117	0.7	138.15	0.2	21.75	145.1	0.2	2.64	BDL
UAS-ST-101112-7	Upper Canyon Rd.	60.1	0.7	137.84	0.2	21.70	116.5	0.3	2.12	BDL
UAS-ST-101112-8	Tesuque	59.8	0.6	138.02	0.2	21.73	130.1	0.2	2.36	BDL
UAS-ST-101112-9	Pojoaque	96.7	0.6	138.16	0.2	21.75	54.90	0.3	1.00	BDL
UAS-ST-101112-10	Nambe 1	776	0.6	137.84	0.1	21.70	56.56	0.2	1.03	BDL
UAS-ST-101112-11	Nambe 2	21.4	0.7	137.88	0.3	21.71	85.91	0.3	1.56	BDL
UAS-ST-101112-12	Nambe 2 <i>duplicate</i>	21.1	0.7	137.95	0.3	21.72	86.20	0.3	1.57	BDL
UAS-ST-101112-13	Santa Cruz	109	0.6	137.90	0.1	21.71	62.66	0.2	1.14	BDL
UAS-ST-101112-14	Española	84.8	0.6	138.16	0.2	21.75	63.63	0.2	1.16	BDL
UAS-ST-101112-15	La Mesilla	261	0.7	137.99	0.2	21.73	62.95	0.3	1.14	BDL
UAS-ST-101112-16	Arroyo Seco	16.6	0.6	138.01	0.2	21.73	64.09	0.2	1.16	BDL
TDMQ water	Field Blank	0.003	0.7	137	2.4	21.57	BDL	--	BDL	BDL

*BDL = below detection limit.

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