

## Appendix H

# DETERMINING SOURCE OF DISSOLVED URANIUM USING ISOTOPES

The isotopic composition of uranium can be used to evaluate whether uranium in surface water and groundwater samples is derived from natural dissolution of uranium-bearing rock units or from anthropogenic activities at uranium mines (Ketterer et al. 2000; Zielinski et al. 1997). Uranium isotopic compositions from a number of studies conducted in the proposed withdrawal area, in Grand Canyon National Park, and along the Colorado River main stem were compiled in Table H-1. Recent technical advances have allowed for the precise measurement of uranium 234 ( $^{234}\text{U}$ ) and uranium 238 ( $^{238}\text{U}$ ) in groundwater and the ability to trace uranium inputs into river systems by comparing the abundance of  $^{234}\text{U}$  with that of  $^{238}\text{U}$  (Luo et al. 2000; Reynolds et al. 2003).

Natural uranium consists of three isotopes,  $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{234}\text{U}$ , with relative abundances of approximately 99.2743%, 0.7200%, and 0.0057%, respectively. Unlike the  $^{235}\text{U}/^{238}\text{U}$  ratio, which exhibits an extremely small range of variation in nature,  $^{234}\text{U}/^{238}\text{U}$  can vary widely in natural waters as a result of processes related to the radioactive decay of daughter  $^{234}\text{U}$  from parent  $^{238}\text{U}$ . These processes result in the preferential mobility of  $^{234}\text{U}$  relative to  $^{238}\text{U}$  during interactions between water and solid phases (Faure and Mensing 2004). Uranium in undisturbed rocks and minerals older than approximately 1 million years reaches a state of radioactive equilibrium in which the rate of decay of the short-lived  $^{234}\text{U}$  is limited by the rate of decay of the long-lived  $^{238}\text{U}$  parent. As a result, the  $^{234}\text{U}/^{238}\text{U}$  activity ratio (AR) is expected to equal unity (defined as secular equilibrium or a value of 1 [Liebe 2003]).

Because variations in the  $^{234}\text{U}/^{238}\text{U}$  activity ratio measured in some environments are very small, isotope ratios can be expressed in delta notation,  $\delta^{234}\text{U}$ , as follows:

$$\delta^{234}\text{U} = (^{234}\text{U}/^{238}\text{U} \text{ AR}_{\text{unknown}} - 1) \times 1,000$$

Delta notation represents a per mil (‰) deviation from a known isotopic reference material, in this case, uranium in secular equilibrium. Materials in secular equilibrium will have  $\delta^{234}\text{U}$  values equal to zero, whereas materials enriched in  $^{234}\text{U}$  will have  $\delta^{234}\text{U}$  values greater than zero. The presence of high levels of uranium sourced from mines will produce waters with  $\delta^{234}\text{U}$  close to secular equilibrium ( $\delta^{234}\text{U} \approx 0$ ), whereas the  $\delta^{234}\text{U}$  values associated with ambient groundwater would typically be much greater than zero.

Bulk dissolution of the solid phase in a chemically aggressive environment (e.g., leachate from fresh mill tailings) results in the release of uranium that has an isotopic composition similar to that of the uranium-enriched rock (i.e., a  $\delta^{234}\text{U} \approx 0$ ). If  $\delta^{234}\text{U}$  values close to zero are detected, the concentration of dissolved uranium is expected to be high because any significant dilution from other sources of water would raise the  $\delta^{234}\text{U}$  value and lower the uranium concentration. In contrast to these conditions, water-rock interaction under less chemically aggressive conditions in natural geomedias (e.g., ambient groundwater) allows preferential incorporation of  $^{234}\text{U}$ , resulting in  $\delta^{234}\text{U}$  values significantly greater than zero. Aquifers containing relatively limited amounts of water and exhibiting long residence times or flow paths will typically have lower  $\delta^{234}\text{U}$  values than aquifers containing abundant water and exhibiting short residence times ( $\ll 1$  million years) because the  $^{234}\text{U}$  activity of the water decreases over time from isotopic decay. In this context, the R-aquifer in the Grand Canyon region contains water representative of short residence times ( $\delta^{234}\text{U} \gg 0$ ): the oldest water age reported for the area, about 22,600 years, was obtained from a well near Williams, Arizona (Bills et al. 2007). Therefore, uncontaminated water from the R-aquifer should have high  $\delta^{234}\text{U}$  values ( $\gg 0$ ).

There are seven sources of the uranium isotopic data given in Table H-1: 1) Woodward-Clyde Consultants (1985), 2) Montgomery and Associates (Montgomery) (1993a, 1993b), 3) Fitzgerald (1996), 4) Liebe (2003), 5) Bills et al. (2010), 6) Sanchez et al. (2010), and 7) USGS National Water Information System (2010). All data were converted to  $\delta^{234}\text{U}$  values for comparison using the equation given above. Review of  $\delta^{234}\text{U}$  values in Table H-1 indicates that four data points from Horn Creek (Fitzgerald 1996; Liebe 2003) fall below secular equilibrium ( $\delta^{234}\text{U} = 0$ ). In rare cases this condition can occur naturally, although it is also likely the result of analytical discrepancies and larger errors from older, less precise analytical techniques. Nevertheless, these data are consistent with leaching from a nearby uranium-rich source, in this case the Orphan Lode Mine. In order to better graphically represent the data, the negative  $\delta^{234}\text{U}$  values have been set to zero; the original data are shown in Table H-1.

**Table H-1.** Dissolved Uranium and  $\delta^{234}\text{U}$  Values for Selected Water Samples

Data Source and Site Description or Name	Sample Date	Dissolved Uranium ( $\mu\text{g/L}$ )	$^{234}\text{U}$ (pCi/L)	$^{238}\text{U}$ (pCi/L)	$^{234}\text{U}/^{238}\text{U}$ (dimensionless)	$\delta^{234}\text{U}$ (dimensionless)	Comment
<b>Montgomery (1993b)</b>							
<b>Western Grand Canyon</b>							
Havasu Spring	5/16/1985	10	3.1	1.6	1.94	938	TMA / ASU data used
	12/18/1985	4	3	1.2	2.50	1,500	TMA / ASU data used
	6/3/1986	4	3.5	1.2	2.92	1,917	TMA / ASU data used
	12/8/1986	4	4.4	2.4	1.83	833	TMA / ASU data used
	5/28/1987	4	4.28	1.45	2.95	1,952	TMA / ASU data used
	12/1/1987	4	3.83	1.55	2.47	1,471	TMA / ASU data used
<b>South Rim, Grand Canyon National Park</b>							
Indian Garden Spring	5/17/1985	2	3.1	0.8	3.88	2,875	TMA / ASU data used
	12/18/1985	6	2.2	0.52	4.23	3,231	TMA / ASU data used
	6/3/1986	3	2.1	0.51	4.12	3,118	TMA / ASU data used
	12/8/1986	3	4.4	1.9	2.32	1,316	TMA / ASU data used
	5/27/1987	4	2.55	0.73	3.49	2,493	TMA / ASU data used
	12/1/1987	2	2.59	0.81	3.20	2,198	TMA / ASU data used; dissolved $^{238}\text{U}$ calculated
<b>Little Colorado River Below Cameron, Arizona</b>							
Blue Spring	5/16/1985	7	4.4	1.8	2.44	1,444	TMA / ASU data used
	12/18/1985	4	4.2	1.3	3.23	2,231	TMA / ASU data used
	6/30/1986	6	3.2	1.7	1.88	882	TMA / ASU data used
	12/8/1986	6	4.2	1.4	3.00	2,000	TMA / ASU data used
	5/28/1987	4	6.09	2.78	2.19	1,191	TMA / ASU data used
	12/1/1987	6	4.44	1.75	2.54	1,537	TMA / ASU data used
<b>Montgomery (1993a)</b>							
<b>Kaibab National Forest</b>							
Canyon Mine Supply Well	12/18/1986	6.0	3.3	1.6	2.06	1,063	TMA / ASU data used
	9/10/1987	5.0	9.03	4.34	2.08	1,081	TMA / ASU data used
	12/1/1987	16.0	11.1	5.53	2.01	1,007	TMA / ASU data used

**Table H-1.** Dissolved Uranium and  $\delta^{234}\text{U}$  Values for Selected Water Samples (Continued)

Data Source and Site Description or Name	Sample Date	Dissolved Uranium ( $\mu\text{g/L}$ )	$^{234}\text{U}$ (pCi/L)	$^{238}\text{U}$ (pCi/L)	$^{234}\text{U}/^{238}\text{U}$ (dimensionless)	$\delta^{234}\text{U}$ (dimensionless)	Comment
<b>Fitzgerald (1996)</b>							
<b>South Rim, Grand Canyon National Park</b>							
Dripping Spring	3/17/1995	1.3	1.65	0.47	3.51	2,511	
Santa Maria Spring	3/17/1995	6.2	4.30	2.21	1.95	946	
Hawaii Spring	3/18/1995	2.6	2.68	0.94	2.85	1,851	
Hermit Source Spring	3/18/1995	2.8	2.89	1.01	2.86	1,861	
Monument Spring	3/18/1995	9.0	6.71	3.24	2.07	1,071	
Cedar Spring	3/18/1995	15.6	10.59	5.57	1.90	901	
Salt Creek	3/19/1995	14.6	8.03	5.23	1.54	535	
Horn Creek	4/30/1994	24.7	8.22	8.76	0.94	0	$\delta^{234}\text{U} = -61.64$ ; zero plotted
	3/19/1995	92.7	27.82	33.21	0.84	0	$\delta^{234}\text{U} = -162.30$ ; zero plotted
	6/5/1995	27.6	9.48	9.9	0.96	0	$\delta^{234}\text{U} = -42.42$ ; zero plotted
Two Springs Creek	4/30/1994	1.8	2.26	0.643	3.51	2,515	
	6/5/1995	1.5	2.16	0.59	3.66	2,661	
Pipe Creek	4/29/1994	2.0	2.04	0.723	2.82	1,822	
	6/4/1995	2.4	2.33	0.85	2.74	1,741	
Burro Spring	4/29/1994	2.5	2.23	0.861	2.59	1,590	
Cremation Creek	6/4/1995	7.6	5.35	2.72	1.97	967	
Sam Magee Spring	6/3/1995	3.8	2.20	1.35	1.63	630	
Lonetree Spring	6/3/1995	4.8	2.71	1.71	1.58	585	
Boulder Creek	6/3/1995	6.9	4.84	2.46	1.97	967	
Grapevine Spring	5/13/1995	1.2	1.54	0.42	3.67	2,667	
Grapevine East Spring	5/13/1995	2.8	1.68	1	1.68	680	
Grapevine Hell Spring	5/13/1995	7.0	4.94	2.5	1.98	976	
Cottonwood Spring	5/12/1995	1.1	1.47	0.41	3.59	2,585	
Cottonwood West Spring	5/13/1995	4.5	3.53	1.6	2.21	1,206	
Page Spring	5/12/1995	3.9	2.24	1.41	1.59	589	
	9/9/1995	3.7	2.09	1.31	1.60	595	
<b>North Rim, Grand Canyon National Park</b>							
Indian Garden Pump Station	4/30/1994	0.2	0.36	0.074	4.81	3,811	
Bright Angel Creek	4/30/1994	0.1	0.82	0.154	5.32	4,318	

**Table H-1.** Dissolved Uranium and  $\delta^{234}\text{U}$  Values for Selected Water Samples (Continued)

Data Source and Site Description or Name	Sample Date	Dissolved Uranium ( $\mu\text{g/L}$ )	$^{234}\text{U}$ (pCi/L)	$^{238}\text{U}$ (pCi/L)	$^{234}\text{U}/^{238}\text{U}$ (dimensionless)	$\delta^{234}\text{U}$ (dimensionless)	Comment
<b>Liebe (2003)</b>							
<b>South Rim, Grand Canyon National Park</b>							
Indian Garden Spring Upstream (I.G. Up)	6/4/2002	3.1	–	–	3.87	2,870	
	6/24/2002	2.9	–	–	3.82	2,820	
	7/15/2002	2.3	–	–	3.80	2,800	
	7/29/2002	2.8	–	–	3.85	2,850	dissolved $^{238}\text{U}$ estimated
Indian Garden Spring Downstream (I.G. Down)	6/4/2002	2.6	–	–	3.83	2,830	
	6/24/2002	2.6	–	–	3.87	2,870	
	7/15/2002	2.4	–	–	3.81	2,810	
	7/29/2002	4.7	–	–	3.76	2,760	
Indian Garden Creek Confluence (I.G. CC)	7/15/2002	1.6	–	–	3.55	2,550	
	7/29/2002	1.4	–	–	3.64	2,640	
Indian Garden - Pipe Creek Mixing Confluence (M.C.)	7/15/2002	1.9	–	–	3.59	2,590	
	7/29/2002	2.4	–	–	3.17	2,170	
Horn Creek Upstream – spring source (Horn Up)	6/4/2002	333	–	–	1.1	100	
	6/24/2002	334	–	–	1.11	110	
	7/15/2002	400	–	–	1.1	100	
	7/29/2002	312	–	–	1.11	110	
Horn Creek Downstream (Horn Down)	6/4/2002	295	–	–	1.11	110	
	6/24/2002	303	–	–	1.1	100	
	7/15/2002	322	–	–	1.11	110	
Horn Creek Alluvium (H.E.A.)	7/29/2002	6	–	–	1.26	260	
Horn Creek West – spring source (Horn West)	7/15/2002	202	–	–	1.01	10	
	7/29/2002	135	–	–	0.99	0	$\delta^{234}\text{U} = -10$ ; zero plotted
Pipe Spring Upstream (Pipe Up)	6/4/2002	3.3	–	–	2.75	1,750	
	6/24/2002	3.1	–	–	2.77	1,770	
	7/15/2002	3.2	–	–	2.75	1,750	
	7/29/2002	2.8	–	–	2.76	1,760	
Pipe Spring Downstream (Pipe Down)	6/4/2002	3.6	–	–	2.72	1,720	
	6/24/2002	3	–	–	2.69	1,690	
	7/29/2002	3.4	–	–	2.71	1,710	
Pipe Creek (Pipe CC)	7/15/2002		–	–	–		
	7/29/2002	23	–	–	1.63	630	

**Table H-1.** Dissolved Uranium and  $\delta^{234}\text{U}$  Values for Selected Water Samples (Continued)

Data Source and Site Description or Name	Sample Date	Dissolved Uranium ( $\mu\text{g/L}$ )	$^{234}\text{U}$ (pCi/L)	$^{238}\text{U}$ (pCi/L)	$^{234}\text{U}/^{238}\text{U}$ (dimensionless)	$\delta^{234}\text{U}$ (dimensionless)	Comment
<b>Liebe (2003), continued</b>							
Burro Spring Upstream (Burro Up)	6/4/2002	4.1	–	–	2.33	1,330	
	6/24/2002	3.5	–	–	2.35	1,350	
	7/15/2002	2.7	–	–	2.38	1,380	
	7/29/2002	3.6	–	–	2.36	1,360	
<b>South Rim, Grand Canyon National Park</b>							
Burro Spring Downstream (Burro Down)	6/4/2002	4.4	–	–	2.34	1,340	
	6/24/2002	4.3	–	–	2.36	1,360	
	7/29/2002	4.4	–	–	2.34	1,340	dissolved $^{238}\text{U}$ estimated
Unnamed Crystalline Core Spring (UCC)	7/29/2002	1.8	–	–	3.33	2,330	
<b>Bills et al. (2010)</b>							
<b>Marble Canyon</b>							
Buck Farm Springs	8/23/2009	2.82	–	–	1.837	837	
Fence Spring	8/20/2009	1.48	–	–	2.623	1,623	
Hanging Spring	8/22/2009	0.62	–	–	4.045	3,045	
Hole-in-the-Wall Spring	8/22/2009	0.6	–	–	4.124	3,124	
Unnamed Spring	8/21/2009	0.6	–	–	4.071	3,071	
<b>House Rock Valley</b>							
South Canyon Spring	8/26/2009	0.82	–	–	3.365	2,365	
Rider Spring	8/25/2009	4.64	–	–	2.625	1,625	
<b>Kanab Plateau – Eastern Margin</b>							
Clear Water Spring	8/28/2009	1.11	–	–	1.523	523	
Upper Jumpup Spring	8/27/2009	3.94	–	–	4.671	3,671	
Lower Jumpup Spring	8/28/2009	7.6	–	–	2.634	1,634	
Mountain Sheep Spring	9/1/2009	8.37	–	–	2.851	1,851	
Schmutz Spring	8/25/2009	4.59	–	–	1.883	883	
Burnt Canyon Well	9/16/2009	3.02	–	–	2.674	1,674	
Tom Land Well	9/14/2009	20.6	–	–	1.749	749	
<b>Kanab Plateau</b>							
Hotel Spring	8/25/2009	2.7	–	–	1.935	935	
Kanab Spring	8/26/2009	4.83	–	–	1.966	966	
Shower Bath Spring	8/26/2009	4.74	–	–	1.893	893	
Side Canyon Spring	8/26/2009	7.44	–	–	1.856	856	
Pineut Well	9/15/2009	2.14	–	–	2.285	1,285	
Slide Spring	8/27/2009	2.83	–	–	5.626	4,626	
Rock Spring	9/2/2009	12.7	–	–	2.459	1,459	
Willow Spring	8/26/2009	19.5	–	–	1.658	658	
<b>Kaibab National Forest</b>							
Canyon Mine Well	9/18/2009	14.4	–	–	2.017	1,017	

**Table H-1.** Dissolved Uranium and  $\delta^{234}\text{U}$  Values for Selected Water Samples (Continued)

Data Source and Site Description or Name	Sample Date	Dissolved Uranium ( $\mu\text{g/L}$ )	$^{234}\text{U}$ (pCi/L)	$^{238}\text{U}$ (pCi/L)	$^{234}\text{U}/^{238}\text{U}$ (dimensionless)	$\delta^{234}\text{U}$ (dimensionless)	Comment
<b>Woodward-Clyde Consultants (1985)</b>							
<b>Marble Canyon</b>							
Spring 1: River Mile 25.3 East	9/19/1982	1.68	1.4	0.57	2.456	1,456	dissolved $^{238}\text{U}$ estimated
Spring 2: River Mile 30.5 East	9/19/1982	1.74	1.6	0.59	2.712	1,712	dissolved $^{238}\text{U}$ estimated
Spring 3: River Mile 30.6 East	9/19/1982	1.51	1.6	0.51	3.137	2,137	dissolved $^{238}\text{U}$ estimated
Spring 4: River Mile 30.8 West	9/19/1982	1.62	1.23	0.55	2.236	1,236	dissolved $^{238}\text{U}$ estimated
Spring 5: River Mile 30.7 West	9/19/1982	1.77	1.48	0.6	2.467	1,467	dissolved $^{238}\text{U}$ estimated
Spring 6: River Mile 30.7 East	9/19/1982	1.95	1.59	0.66	2.409	1,409	dissolved $^{238}\text{U}$ estimated
Spring 7: River Mile 35.0 West	9/19/1982	0.97	0.91	0.33	2.758	1,758	dissolved $^{238}\text{U}$ estimated
Spring 9: River Mile 31.2 West	9/19/1982	1.30	0.86	0.44	1.955	955	dissolved $^{238}\text{U}$ estimated
<b>USGS (2010b)</b>							
<b>Kaibab National Forest</b>							
355308112054101 (Canyon Mine Well)	5/20/2003	13.31	9.2	4.51	2.040	1,040	dissolved $^{238}\text{U}$ estimated
<b>Coconino Plateau</b>							
353930112075001 (Valle Well; A-26-02 01CDD)	4/13/2004	14.76	8.4	5	1.680	680	dissolved $^{238}\text{U}$ estimated
<b>Havasupai Reservation</b>							
361303112411200 (Havasupai Spring; B-33-04 26)	8/23/1994	4	2.9	1.1	2.636	1,636	
361524112420400 (Havasupai Spring below Supai; B-33-04 11)	8/24/1994	4	3.6	1.2	3.000	2,000	
361352112413201 (Supai Well; B-33-04 22)	8/23/1994	3.00	3.7	1.4	2.643	1,643	
<b>Western Grand Canyon</b>							
9404200 (Colorado River above Diamond Creek)	3/13/2001	3.45	2	1.1	1.818	818	
	8/28/2001	3.8	2.1	1.2	1.750	750	
	8/14/2002	3.71	2.2	1.2	1.833	833	
	11/23/2004	4.76	2.45	1.44	1.701	701	
<b>Sanchez et al. (2010)</b>							
<b>Colorado</b>							
Colorado River at Grand Lake	8/4/2007	0.04	–	–	1.288	288	
	7/20/2008	0.15	–	–	1.154	154	
	8/6/2009	0.23	–	–	1.498	498	
Colorado River at State Bridge	8/6/2009	0.6	–	–	1.521	521	

**Table H-1.** Dissolved Uranium and  $\delta^{234}\text{U}$  Values for Selected Water Samples (Continued)

Data Source and Site Description or Name	Sample Date	Dissolved Uranium ( $\mu\text{g/L}$ )	$^{234}\text{U}$ (pCi/L)	$^{238}\text{U}$ (pCi/L)	$^{234}\text{U}/^{238}\text{U}$ (dimensionless)	$\delta^{234}\text{U}$ (dimensionless)	Comment
<b>Sanchez et al. (2010), continued</b>							
<b>Colorado</b>							
Colorado River at De Bisque	8/3/2007	1.59	–	–	1.6	600	
Colorado River at Fruita	7/18/2008	2.78	–	–	1.636	636	
	8/6/2009	2.97	–	–	1.655	655	
<b>Utah</b>							
Colorado River above Moab (Moab Up)	8/2/2007	5.28	–	–	1.591	591	
	8/8/2009	2.86	–	–	1.721	721	
Colorado River below Moab (Moab Down)	8/2/2007	6.09	–	–	1.551	551	
	7/17/2008	2.69	–	–	1.67	670	
	8/8/2009	2.96	–	–	1.722	722	
<b>Arizona, upstream from Grand Canyon</b>							
Colorado River at Lees Ferry	7/31/2007	3.59	–	–	1.549	549	
	7/15/2008	3.22	–	–	1.523	523	
	7/4/2009	1.43	–	–	1.68	680	
<b>Western Grand Canyon</b>							
Colorado River at Diamond Creek	6/29/2008	3.12	–	–	1.725	725	
	6/20/2009	2.32	–	–	1.861	861	
<b>Arizona, Lower Colorado River</b>							
Colorado River at Willow Beach	7/29/2007	4.51	–	–	1.769	769	
	6/29/2008	4.24	–	–	1.7	700	
	6/19/2009	2.38	–	–	1.704	704	

## Notes:

 $\mu\text{g/L}$  = micrograms per liter

TMA = Thermo Analytical, Inc., Richmond, California

pCi/L = picoCuries per liter

ASU = Arizona State University

USGS = U.S. Geological Survey

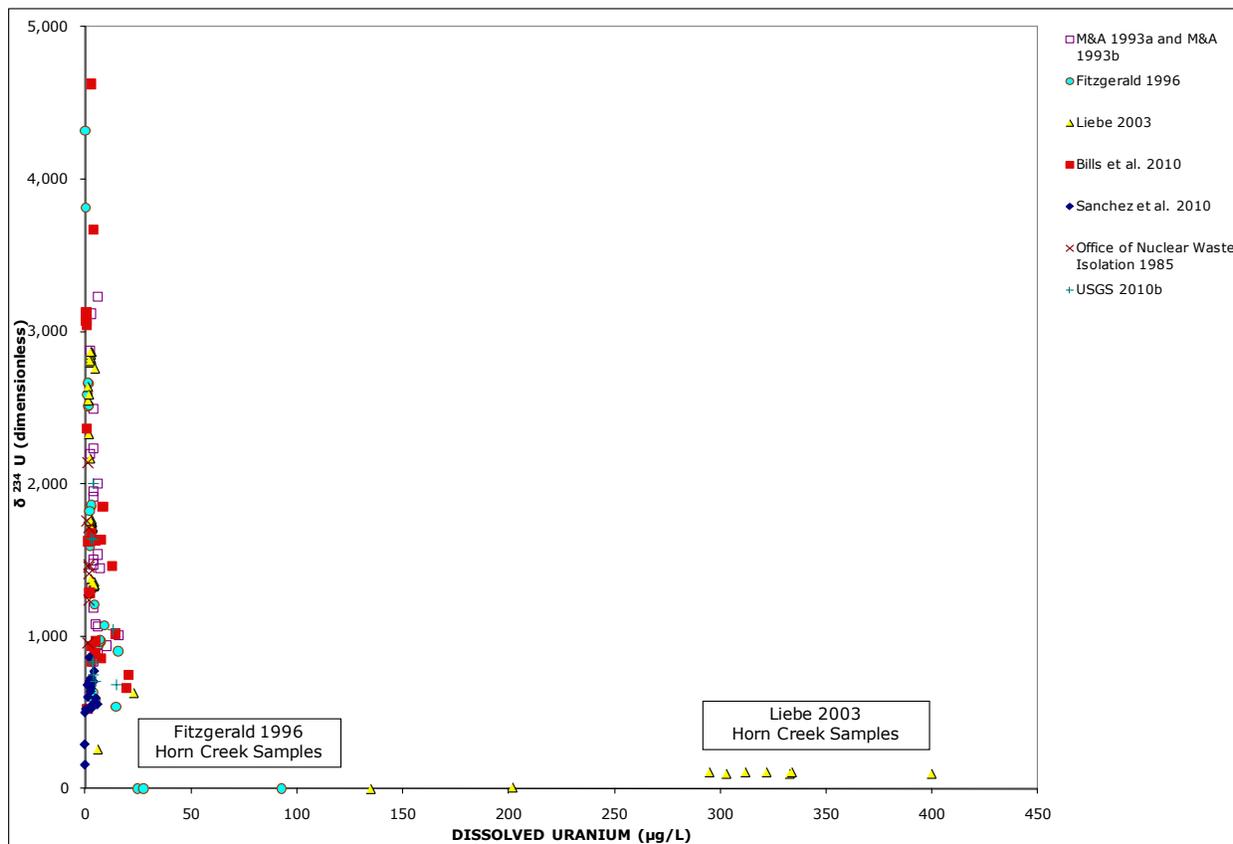
 $^{234}\text{U}/^{238}\text{U}$  = ratio of isotope 234 to 238

– = not reported

 $\delta^{234}\text{U}$  = delta calculated using  $(^{234}\text{U}/^{238}\text{U} - 1) \times 1,000$ 

All sample results are plotted on Figure H-1, and a subset of data with  $\delta^{234}\text{U}$  values less than 1,000 is shown in Figure H-2. The large variations in  $\delta^{234}\text{U}$  are readily apparent, despite the significantly higher analytical errors associated with the older data sets. Most of these data have  $\delta^{234}\text{U}$  values greater than 500 and dissolved uranium concentrations of less than 20  $\mu\text{g/L}$ . These data are indicative of natural weathering processes because the  $\delta^{234}\text{U}$  of these samples is much greater than zero and the concentration of dissolved uranium is not elevated substantially above ambient levels (about 7  $\mu\text{g/L}$ ). The only results that clearly indicate anthropogenic effects are those for samples obtained from Horn Creek springs; these results have both high concentrations of dissolved uranium and low  $\delta^{234}\text{U}$  values that are near or below

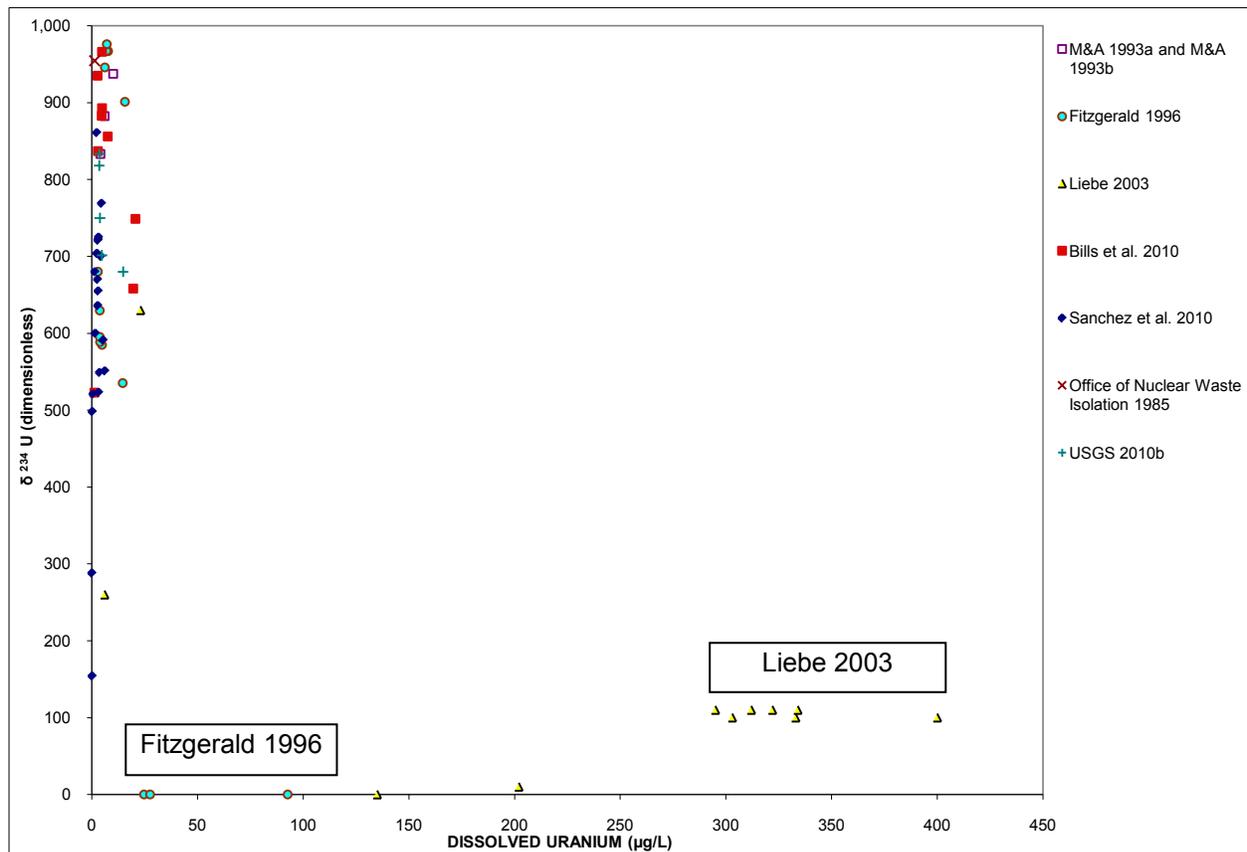
secular equilibrium. These elevated uranium concentrations, combined with low  $\delta^{234}\text{U}$  values, are associated with data reported by Fitzgerald (1996) and Liebe (2003) and are most likely indicative of surface water and/or perched groundwater interacting with the unreclaimed mine workings of the Orphan Lode Mine, which is located about 0.5 mile southwest of the springs sampled by Liebe (2003). This impacted water appears to move from the mine workings downward (about 500 vertical feet) via fractures in the Supai Group and into the Redwall and Muav limestones, where it experiences minimal dilution or attenuation while traveling the short distance to Horn Creek. The hypothesis that Horn Creek is influenced by uranium derived from mining is also supported by the higher sulfate content of these waters, presumably as a result of oxidation of associated sulfide ores, compared with other study sites (Liebe 2003).



**Figure H-1.**  $\delta^{234}\text{U}$  for selected water samples: graph of dissolved uranium versus  $\delta^{234}\text{U}$  from 0 to 5,000.

Natural erosion of the exposed Orphan Lode breccia pipe in the tributary canyon of the mine or of waste materials dumped into the canyon would not likely result in a  $^{234}\text{U}/^{238}\text{U}$  activity ratio near 1 in the water sampled by Liebe (2003), which together with the elevated uranium concentrations indicates an anthropogenic source. It should be emphasized that Liebe (2003) sampled the “Horn up” location on four occasions in June and July 2002, one of the worst recent drought years, when discharge was likely groundwater baseflow unaffected by surface water runoff, and obtained comparable results ranging from 312 to 400  $\mu\text{g/L}$ . Further, Liebe (2003) obtained two water samples directly from another spring at the Redwall-Muav limestone contact (“Horn west”) in the next tributary canyon west of the tributary canyon below the mine. These two canyons, which are both tributary to Horn Creek, are separated by a surface water divide and a large outcrop of the Redwall Limestone (Liebe 2003). The uranium concentrations detected in the two “Horn west” samples were 135 and 202  $\mu\text{g/L}$ . The  $^{234}\text{U}/^{238}\text{U}$  activity ratio for both of these sampling locations is near 1, which together with the elevated uranium concentrations indicates

anthropogenic sources. Both the “Horn up” and “Horn west” samples were collected at the spring source at the Redwall-Muav contact, as reported by Liebe (2003).



**Figure H-2.**  $\delta^{234}\text{U}$  for selected water samples: graph of dissolved uranium versus  $\delta^{234}\text{U}$  from 0 to 1,000.

The Horn Creek drainage area includes the Orphan Lode Mine, which was in production from 1956 to 1969 and is not part of current mining or exploration activity (U.S. Energy Information Administration 2005). The Orphan Lode Mine is currently a federal Superfund site, and Grand Canyon National Park has posted signs on Horn Creek warning the public not to drink the surface water because of potentially hazardous levels of radioisotopes. Monitoring for uranium isotopes alone, or combined with monitoring for uranium, strontium, and lead isotopes, provides an appropriate basis for distinguishing anthropogenic from natural weathering effects, as reflected in isotopic data for the Orphan Lode Mine and other breccia pipe uranium deposits (Gornitz and Kerr 1970; Ludwig and Simmons 1992).

In many cases, isotope mixing plots (e.g.,  $\delta^{234}\text{U}$  versus reciprocal U concentrations) can be used to indicate the source(s) of uranium contamination and the potential mixing relations between contaminated groundwater (high uranium concentrations and low  $\delta^{234}\text{U}$  values) and ambient groundwater (low uranium concentrations and high  $\delta^{234}\text{U}$  values), if the data collected are from the same flow system and are available at varying distances from high-impact areas. However, given the varied analytical methods and wide temporal and spatial differences in the current data set, such analyses would be highly speculative and are not appropriate for the EIS.

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