Appendix A

NORTHERN ARIZONA UNIVERSITY

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FROM: Michael E. Ketterer, Ph.D., Professor, Chemistry and Biochemistry
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SUBJECT: Results for the determination of $^{234}U/^{238}U$ Activity ratios and U concentrations in your Tuba City Vicinity water samples by Quadrupole ICPMS

I am pleased to provide results for the determination of $^{234}U/^{238}U$ activity ratios and U concentrations in your 60 water and leachate samples from the Tuba City (AZ) vicinity. These samples were received in my laboratory on March 27, 2009.

Analytical Procedures: For most samples, a 10 mL aliquot was taken for analysis; this was pipetted volumetrically into a 90 mL polystyrene beaker. For several samples, 5 mL or 8 mL aliquots were used on account of limited available sample volumes. Trace metal grade nitric acid (16 M, 1 mL) was added. Thereafter, ^{233}U spike (149.6 pg U, prepared from IRMM-057, 99.96% ^{233}U) was added. The samples were allowed to stand for several hours to allow sample-spike equilibration. Uranium was chemically isolated using TRU resin (EIChrom, Lisle, IL, Part No. TR-B50-S, 50-100 μm). 25 mg of TRU resin beads were added to each sample, and the mixtures were agitated manually for 2 hours. The resin beads were collected on a 10 mL pipet tip equipped with a glass wool plug to retain the resin, forming a "column" of resin. The colums were rinsed 3x with 1 mL 2 M HNO_3, 3x with 1 mL 1 M HCl, and 3x with 1 mL 2 M HNO_3. The column rinses remove matrix elements and any Th that could form ThH^+ and interfere with mass spectrometric measurements of ^{233}U. Uranium is eluted from the TRU columns using the following sequence: 0.4 mL water, 0.4 mL 0.05 M ammonium oxalate, and 0.4 mL water. The U fractions were further diluted to 2 mL with water before analysis. Blanks (n=5) were prepared and run through the entire sample preparation process. Duplicates of six samples were prepared and run through the entire sample preparation process.

ICPMS analyses were conducted with a Thermo X Series II quadrupole ICPMS. The instrument is equipped with an APEX HF sample introduction system (ESI Scientific, Omaha, NE) for efficient aerosol transport. The U fractions were analyzed either as-is, or diluted with water to attenuate the $^{235}U^+$ ion beam. The ICPMS was operated in a peak-jump mode (10 ms dwell, 1 measurement at the summit of each peak, 2000 sweeps per integration). Ions monitored were ^{232}Th, ^{233}U, ^{234}U, and ^{235}U. Each integration required 92 seconds and a block of three sequential integrations were collected for each sample (the averages and standard deviations reported are the average of these three integrations). The sample introduction system was rinsed between samples with an aqueous solution containing 0.005 M ammonium oxalate and 0.1 M HNO_3; the $^{235}U^+$ ion beam was monitored to ensure rinse-out to the signal levels typical of the blanks. The preparation blanks were analyzed in undiluted fashion (2 mL) or diluted to larger volumes (6, 10,

15, or 40 mL); the average blank results were used to perform subtractions at m/z 234 and 235. The $^{233}U^{+}$ signal was corrected for the small levels of ThH^{+} using the measured ThH^{+}/Th^{+} factor, though this correction was found to be immaterial after TRU separation. Mass bias corrections were performed using an externally measured value of $^{238}U/^{235}U$ in a naturally occurring U solution.

The blank-subtracted, mass bias-corrected $^{234}U/^{235}U$ atom ratios were converted to $^{234}U/^{238}U$ activity ratios as follows:

$$AR_{234238} = (^{234}U/^{235}U) * (1 / 137.88) / 0.00005472$$

where (1 / 137.88) is the $^{235}U/^{238}U$ atom ratio in Nature (constant within 0.1%) and 0.00005472 is the $^{234}U/^{238}U$ atom ratio at secular equilibrium.

Seven blocks of $^{234}U/^{235}U$ atom ratios were collected at different times during the analysis for a U solution prepared from "modern coral". This material has the activity ratio characteristic of modern seawater (1.148 ± 0.002).

The uranium concentrations in the water and leach samples were calculated using the ^{233}U and ^{235}U ion intensities (with appropriate ThH^{+} correction and blank subtraction). Standard isotope dilution calculations were utilized.

Results are tabulated below.

Modern Coral AR Results

Block	AR 234/238	SD	
1	1.146	0.001	
2	1.144	0.007	
3	1.152	0.005	
4	1.147	0.003	
5	1.142	0.004	
6	1.142	0.001	
7	1.142	0.005	
AVG	**1.145**		
SD	**0.004**		

The expected AR in modern seawater is 1.148 +/- 0.002.

These results indicate excellent agreement between our AR_{234238} values and the expected results for modern seawater, and argue against significant systematic errors in the activity ratio data.

Sample (Preparation + Measurement) Duplicates Results

		Prep #1		Prep #2	
My Lab ID	**Your ID**	**AR 234/238**	**SD**	**AR 234/238**	**SD**
1	B12	2.128	0.003	2.128	0.009
6	MW-14	1.676	0.016	1.669	0.012
18	B24-1 TCLP	1.668	0.008	1.664	0.010
26	B29-5 TCLP	1.905	0.006	1.892	0.002
54	W-1-20a	1.645	0.012	1.677	0.016
60	TC08SS06a	1.706	0.007	1.722	0.017

		Prep #1		Prep #2	
My Lab ID	**Your ID**	**U, ug/L**	**SD**	**U, ug/L**	**SD**
1	B12	25.89	0.06	27.78	0.06
6	MW-14	19.66	0.07	19.85	0.02
18	B24-1 TCLP	8.82	0.01	8.77	0.13
26	B29-5 TCLP	14.13	0.02	13.77	0.02
54	W-1-20a	0.66	0.00	0.75	0.00
60	TC08SS06a	3.40	0.00	3.39	0.01

The duplicate results indicate relatively good agreement for both the activity ratios and U concentrations.

Sample results follow. I note that my measurements of U concentrations are systematically 10-20% higher than you have reported to me in the USGS laboratory report of March 24, 2009 (MRP-08694). Several possibilities exist for this discrepancy, which I can check on. It may be that this is a result of evaporation of the samples, though the deviations seem excessive. I ma fairly confident that are pipet delivery (water sample volume) errors are relatively small, as these are checked gravimetrically. Though I have had no problems to date with the ^{233}U spike solution, I will check its calibration against some ^{238}U primary standard chemicals (and if necessary, revise the U concentration data); this would seem to be the first obvious place to investigate.

My Lab ID	Your ID	AR 234/238	SD	U, ug/L	SD
1	B12	2.128	0.003	25.89	0.06
2	B15	2.154	0.009	14.98	0.02
3	B29	2.201	0.004	23.82	0.03
4	B33	2.134	0.004	107.45	0.14
5	B34	2.055	0.012	27.58	0.05
6	MW-14	1.676	0.016	19.66	0.07
7	WP-5	2.046	0.013	17.82	0.04
8	WP-8	1.836	0.009	80.49	0.48
9	WP-10	2.085	0.002	50.19	0.11
10	MW-29	2.027	0.010	49.27	0.13
11	B12-10 TCLP	2.071	0.002	3.36	0.01
12	B33-13 TCLP	2.065	0.005	3.06	0.01
13	B12-11 TCLP	2.167	0.017	2.62	0.00
14	B29-1 TCLP	1.296	0.045	0.42	0.00
15	B29-7 TCLP	1.938	0.016	3.32	0.00
16	B29-2 TCLP	1.512	0.031	0.74	0.00
17	B33-2 TCLP	1.850	0.005	5.52	0.01
18	B24-1 TCLP	1.668	0.008	8.82	0.01
19	W-1-35 TCLP	1.547	0.012	2.36	0.01
20	B29-3 TCLP	1.762	0.001	3.35	0.01
21	B12-4 TCLP	2.038	0.005	22.78	0.06
22	B29-6 TCLPd	1.919	0.007	14.89	0.03
23	B15-4 TCLP	2.074	0.009	4.55	0.00
24	B15-4 TCLPd	2.074	0.009	4.85	0.01
25	B33-6 TCLP	2.032	0.002	10.53	0.01
26	B29-5 TCLP	1.905	0.006	14.13	0.02
27	B29-4 TCLP	1.892	0.014	7.80	0.01
28	B12-5 TCLP	2.058	0.011	22.41	0.05
29	TCSS02-TCLP	1.870	0.013	17.22	0.03
30	W-1-25 TCLP	1.686	0.004	60.35	0.04
31	B29-6 TCLP	1.916	0.004	14.14	0.03
32	B10-4 TCLP	2.032	0.002	19.52	0.02
33	TC-RK-02B-a	1.429	0.056	0.23	0.00
34	TC08B12-4Ad	1.965	0.005	2.08	0.00
35	TC-RK-02D-a	1.371	0.026	0.34	0.00
36	TCLFB33-2a	1.954	0.030	0.44	0.00
37	TC08B15-3a	1.879	0.034	0.37	0.00
38	TC08B15-2a	1.815	0.031	2.28	0.01
39	TCLFB33-1a	1.861	0.013	6.90	0.05
40	TCLFB29-3b	1.809	0.009	1.14	0.01
41	TCLFB29-6b	1.946	0.050	0.73	0.00
42	TC08B15-1a	1.255	0.033	0.88	0.01
43	TCLFB29-5b	1.761	0.026	1.90	0.01
44	TCLFB29-4b	1.839	0.034	2.48	0.00
45	B24-1a	1.636	0.033	0.50	0.00
46	WP7-2a	1.317	0.017	0.40	0.05
47	TCLFB29-11a	2.047	0.053	0.29	0.00

48	TCLFB29-8a	1.904	0.039	0.31	0.00
49	TC08B12-5a	1.992	0.046	1.46	0.01
50	TC08B10-4a	2.038	0.024	1.00	0.00
51	TC08B12-4a	1.902	0.024	3.28	0.01
52	WP7-1a	1.473	0.085	0.21	0.00
53	TC08SS02a	1.737	0.046	1.63	0.00
54	W-1-20a	1.645	0.012	0.66	0.00
55	W-1-25a	1.646	0.046	3.00	0.05

Please let me know if you have any questions. I will look forward to working with you on any additional analysis of samples.

Prepared by: Michael E. Kott

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