GSA Data Repository Item 2020023

Paces, J.B., Palmer, M.V., Palmer, A.N., Long, A.J., and Emmons, M.P., 2019, 300,000 yr history of water-table fluctuations at Wind Cave, South Dakota, USA—Scale, timing, and groundwater mixing in the Madison Aquifer: GSA Bulletin, https://doi.org/10.1130/B35312.1.

Data Repository

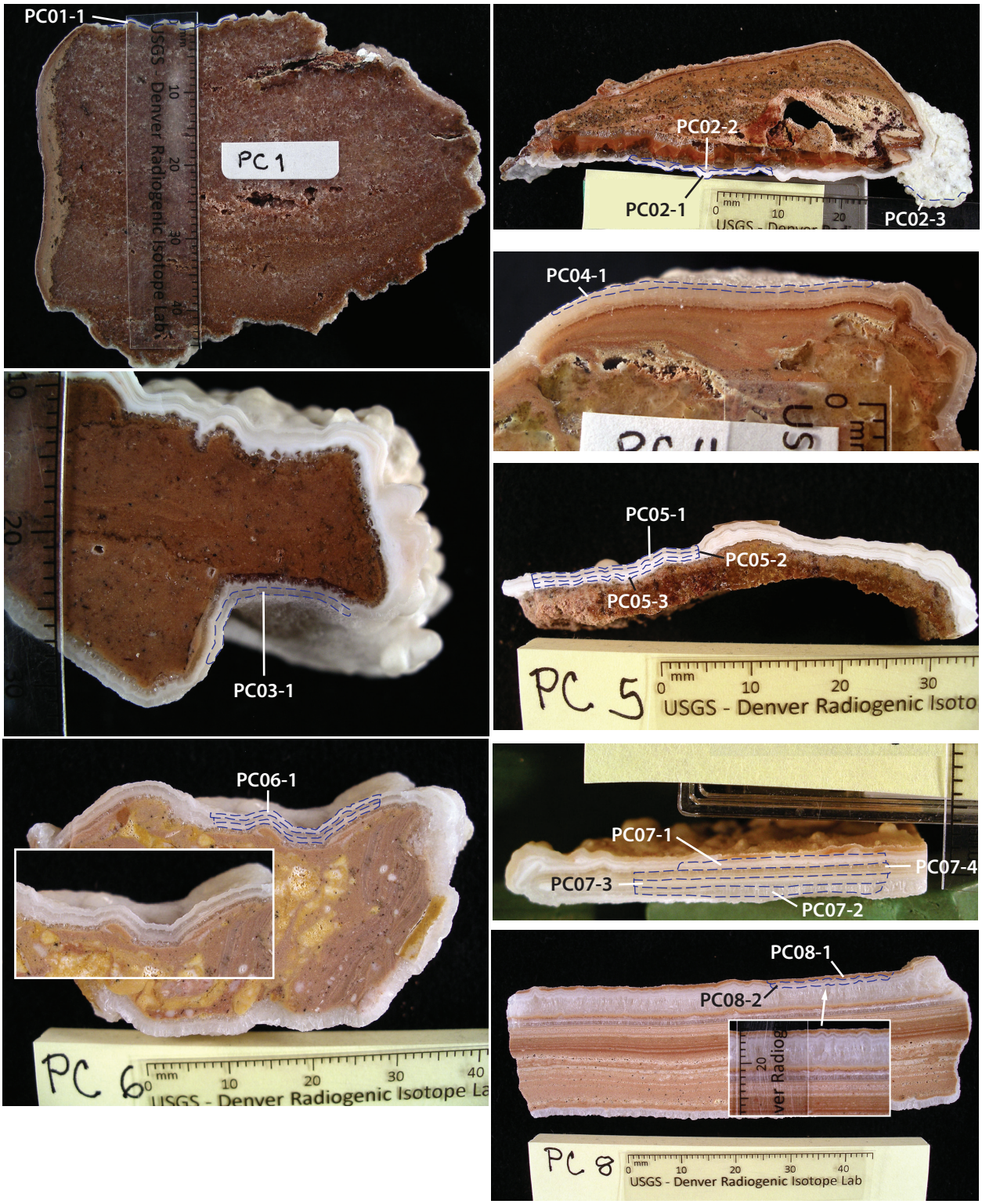
Photographs of Wind Cave Specimens showing subsampling locations S2

U-Th and Sr Analytical Methods S8

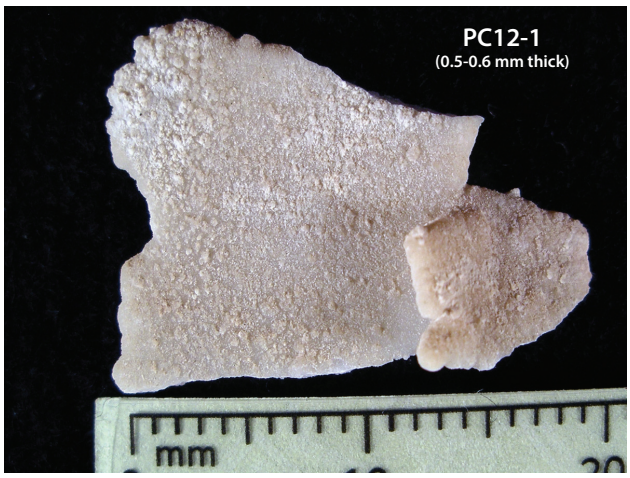
Table S1. U-Th concentrations and isotope data for Wind Cave speleothems S10

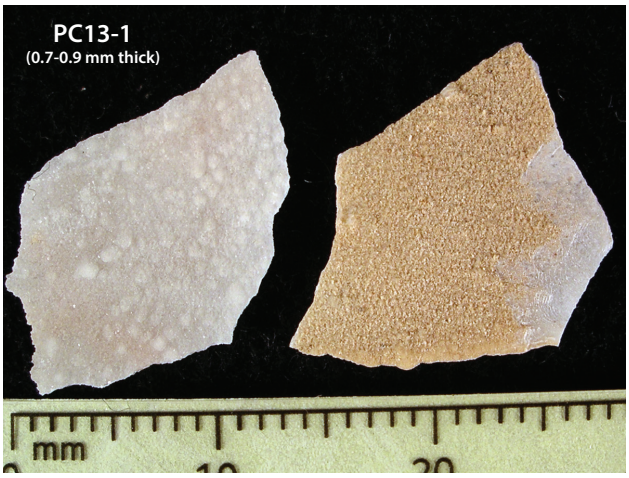
Table S2. Collection dates, locations, and aquifer classifications for water samples near Wind Cave National Park S13

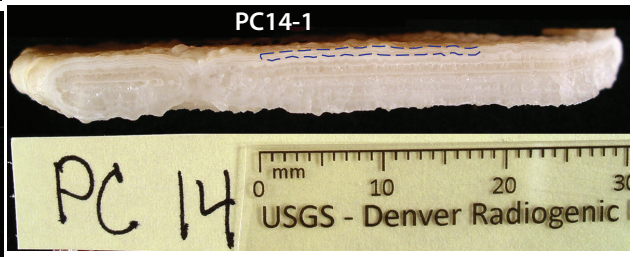
References S14


PC01-1
PC 1
USGS - Denver Radiogenic Isotope Lab
PC02-2
PC02-1
PC02-3
PC04-1
PC03-1
PC05-1
PC05-2
PC05-3
PC 5
USGS - Denver Radiogenic Isoto
PC06-1
PC 6
USGS - Denver Radiogenic Isotope La
PC07-1
PC07-4
PC07-3
PC07-2
PC08-1
PC08-2
PC 8
USGS - Denver Radiogenic Isotope Lab

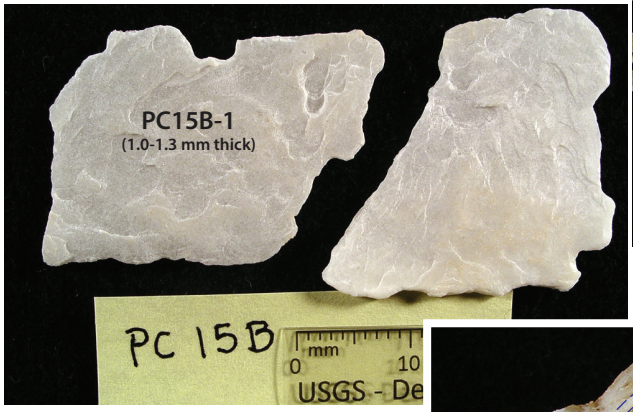
PC09C-1
(0.85-1.1 mm thick)

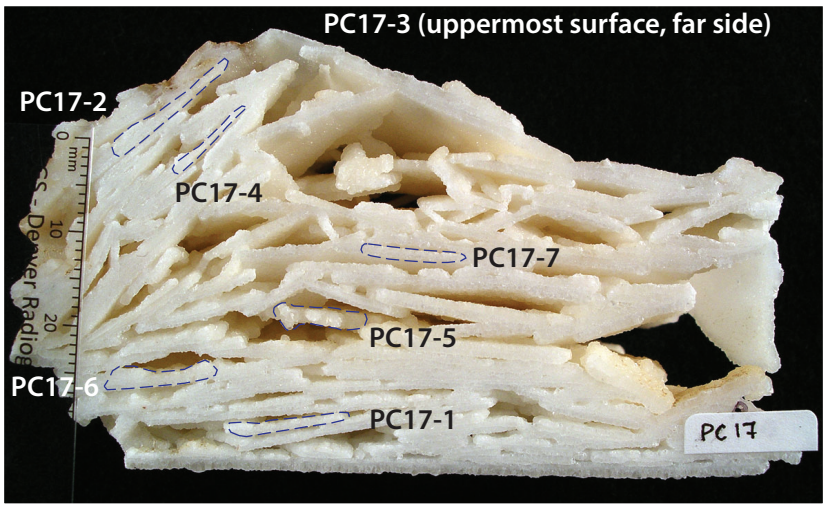

PC12-1
(0.5-0.6 mm thick)

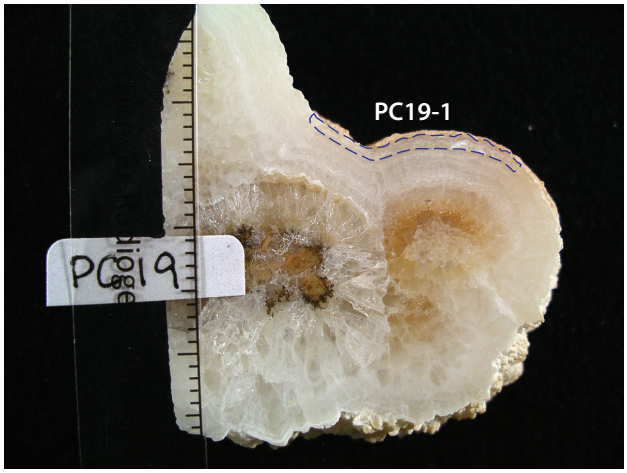

PC13-1
(0.7-0.9 mm thick)

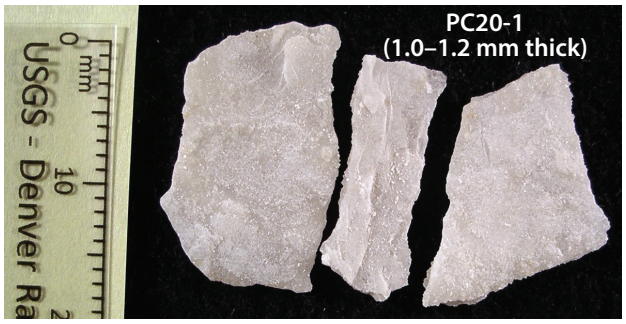

PC14-1
PC 14
USGS - Denver Radiogenic

PC16-1
(<0.5 mm thick)

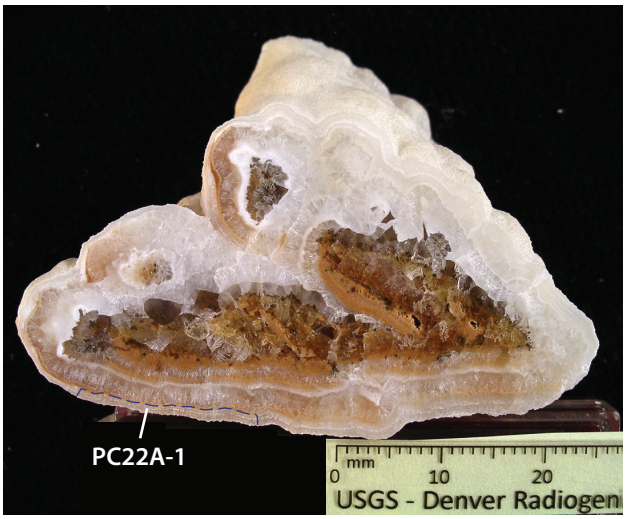

PC15B-1
(1.0-1.3 mm thick)
PC 15B

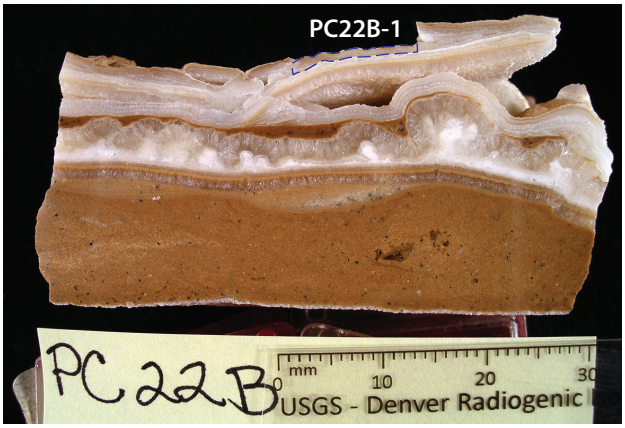

PC17-3 (uppermost surface, far side)
PC17-2
PC17-4
PC17-7
PC17-5
PC17-6
PC17-1
PC 17

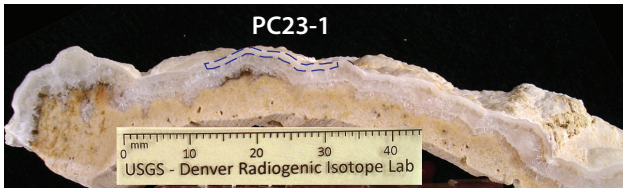

PC19-1
PC19

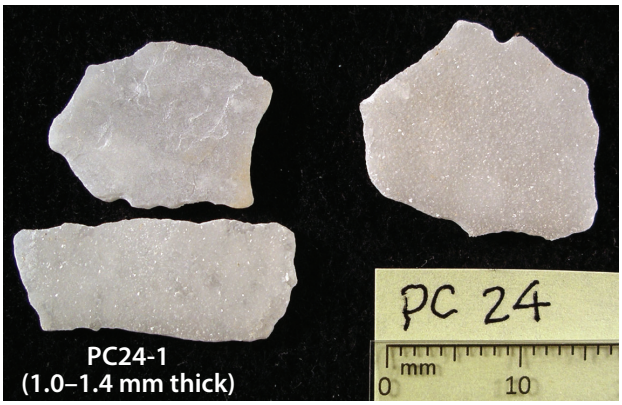

PC20-1
(1.0–1.2 mm thick)
USGS - Denver Ra

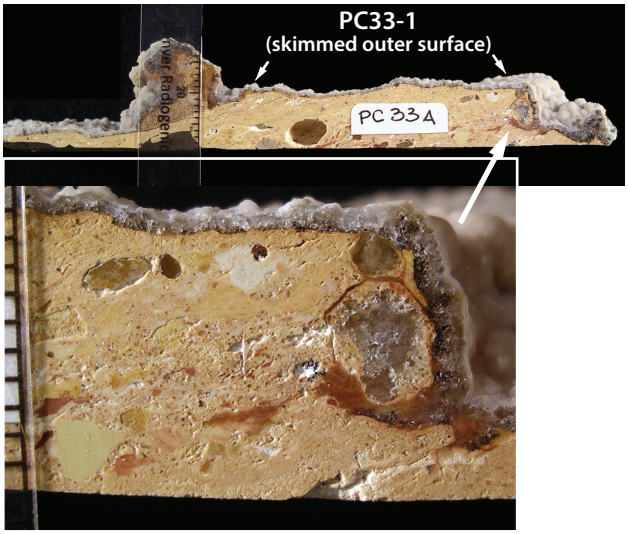
PC21-1
(<0.5 mm thick)
mm

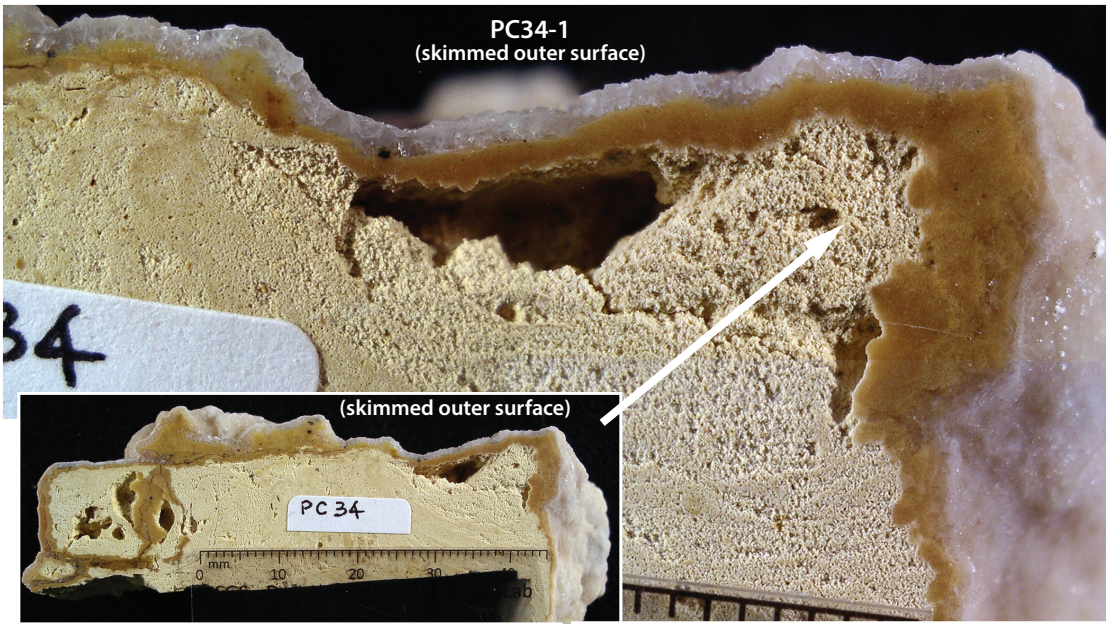

PC22A-1
USGS - Denver Radiogen

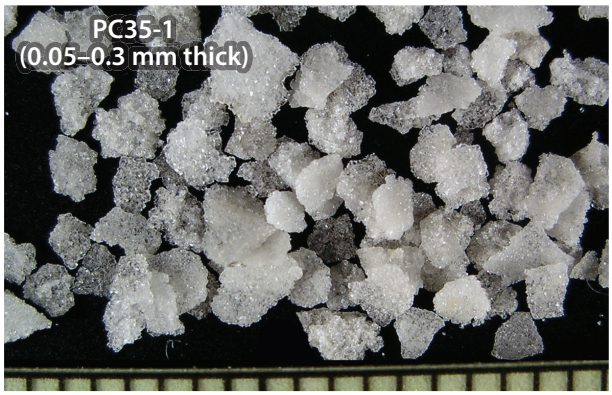

PC22B-1
PC 22B
USGS - Denver Radiogenic

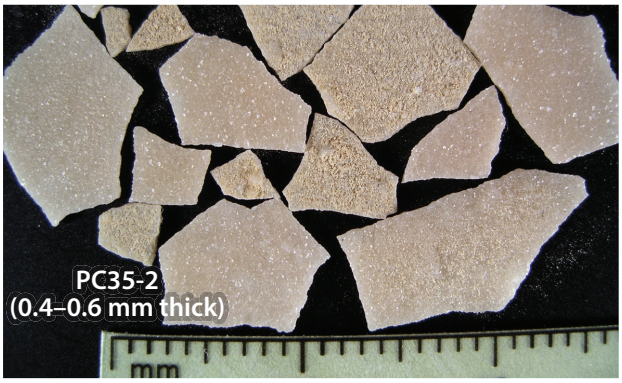

PC23-1
USGS - Denver Radiogenic Isotope Lab

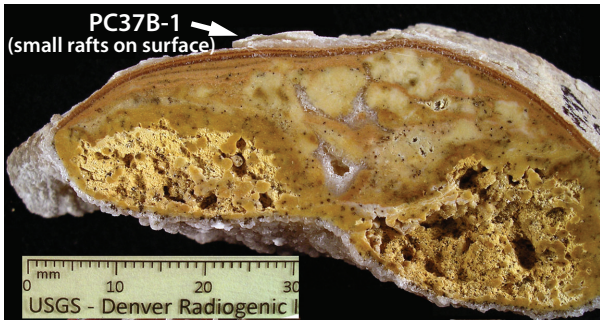

PC24-1
(1.0–1.4 mm thick)
PC 24

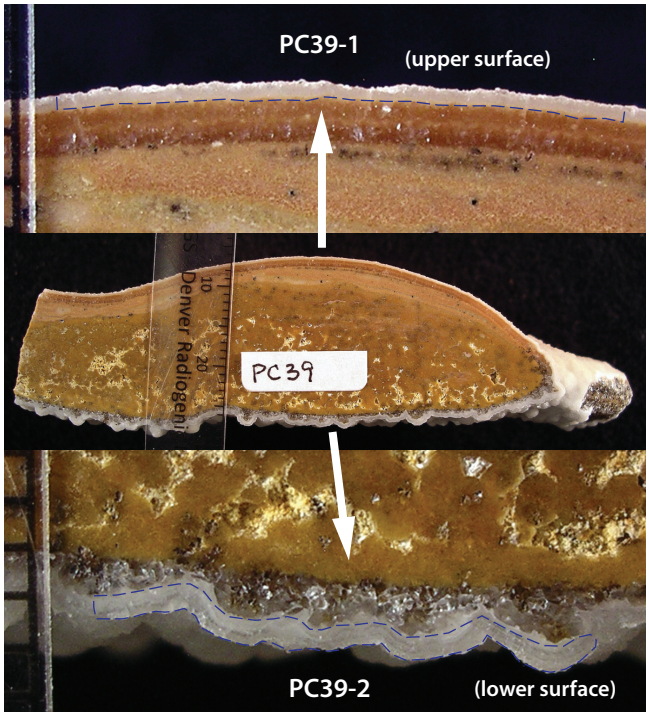

PC33-1
(skimmed outer surface)
PC 33A

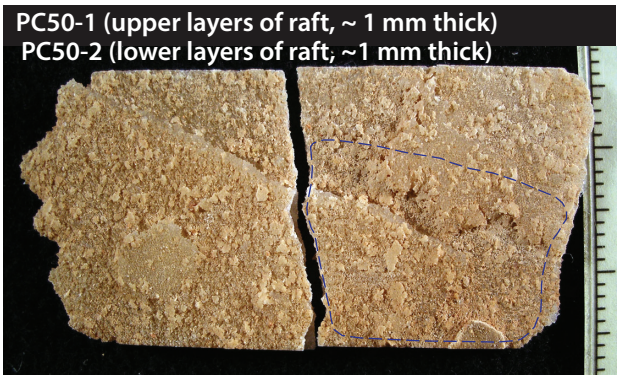

PC34-1
(skimmed outer surface)
(skimmed outer surface)
PC 34

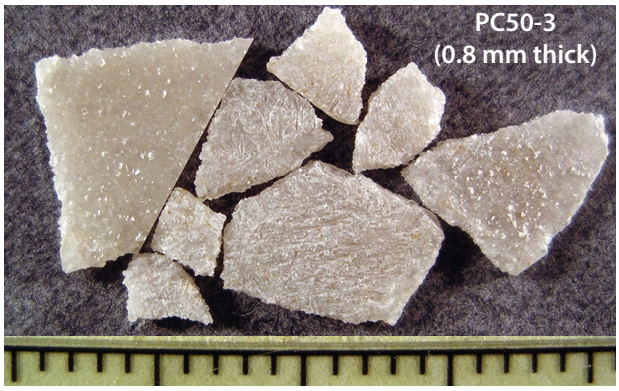

PC35-1
(0.05–0.3 mm thick)

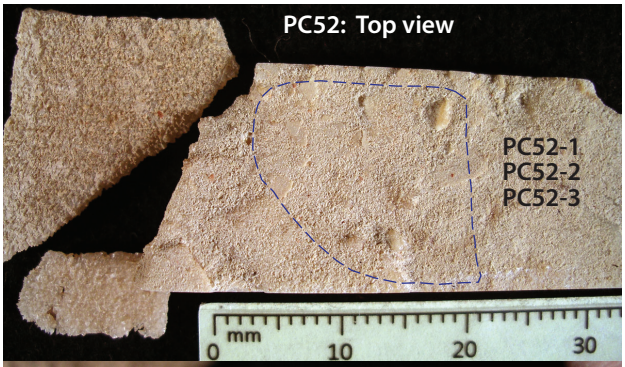

PC35-2
(0.4–0.6 mm thick)
mm

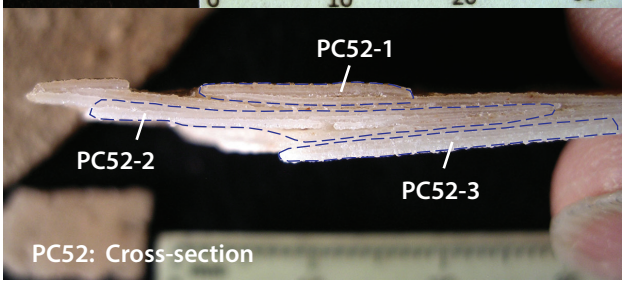

PC37B-1
(small rafts on surface)
USGS - Denver Radiogenic

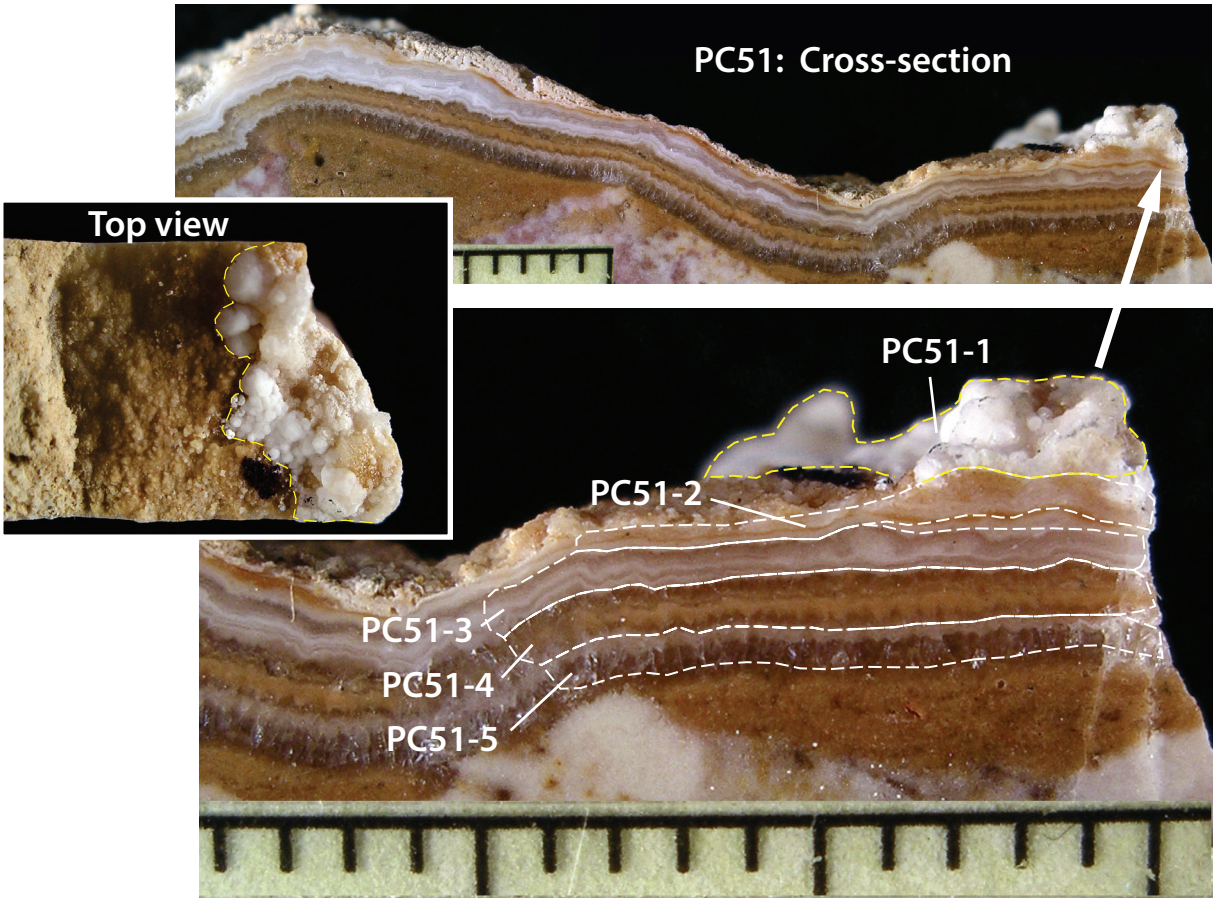

PC39-1
(upper surface)
PC39
PC39-2
(lower surface)

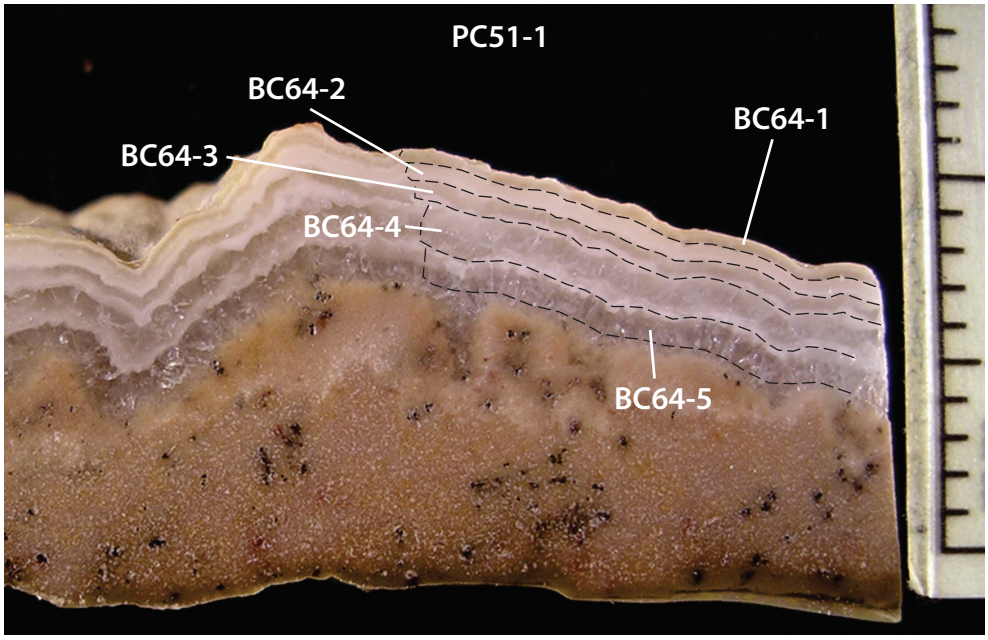

PC50-1 (upper layers of raft, ~ 1 mm thick)
PC50-2 (lower layers of raft, ~1 mm thick)

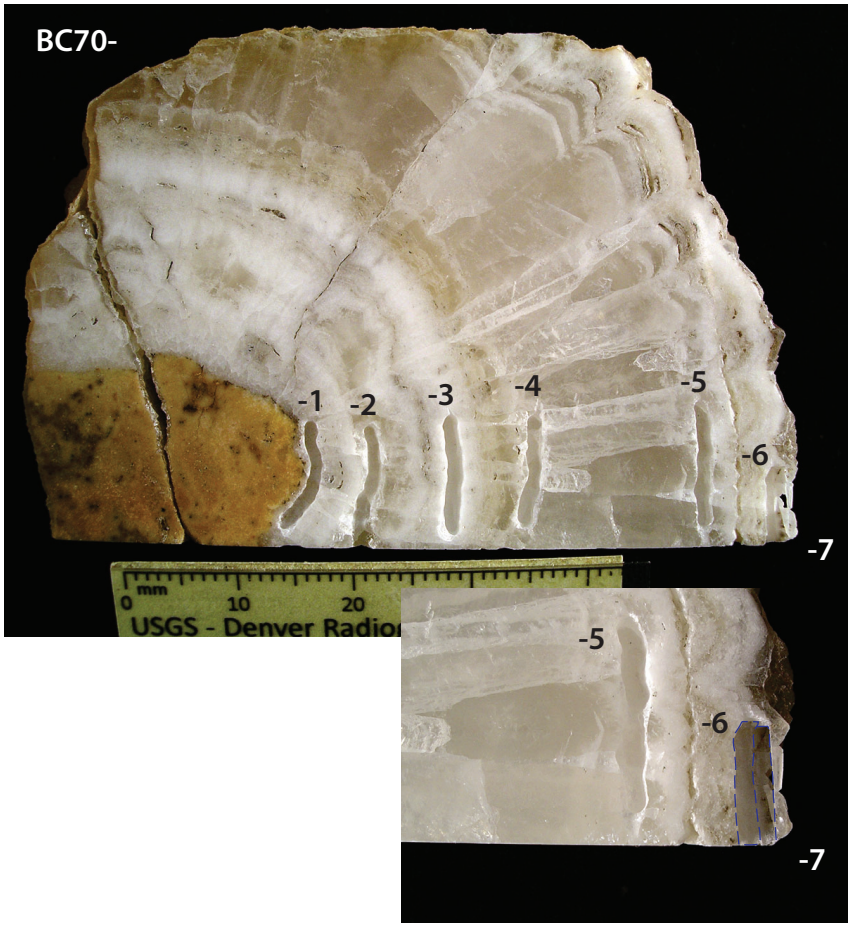

PC50-3
(0.8 mm thick)


PC52: Top view
PC52-1
PC52-2
PC52-3
mm
0
10
20
30


PC52-1
PC52-2
PC52-3
PC52: Cross-section


PC51: Cross-section
Top view
PC51-1
PC51-2
PC51-3
PC51-4
PC51-5


PC51-1
BC64-2
BC64-1
BC64-3
BC64-4
BC64-5


BC70-
-1
-2
-3
-4
-5
-6
-7
mm
0
10
20
USGS - Denver Radio
-5
-6
-7

U-Th and Sr Analytical Methods

Data in this report were determined at USGS laboratories in Denver, CO. Powdered speleothem subsamples were weighed in 7-ml Teflon® PFA vials, then wetted with deonized water. High-purity nitric acid was added to digest the carbonate fraction of the samples followed by addition of a weighed amounts of a highly purified mixed U-Th tracer solution with known quantities of ^{236}U, ^{233}U, and ^{229}Th. Vials were capped, heated overnight on a 120°C hotplate, then taken to dryness under dry-nitrogen gas flow. Digested salts were dissolved and equilibrated in 7N nitric acid. Samples were centrifuged at 10,000 rpm and the supernate was transferred to a second vial. Any remaining residue was transferred back to the original vials using concentrated hydrofluoric and nitric acids and allowed to digest overnight on a 120°C hotplate. After evaporation, all residue dissolved in 7N nitric acid, which was added to the original digestion. Therefore, all analyses were made on total digestions of the samples to eliminate laboratory fractionation of U and Th. Sr analyses were made on the same digestions.

Standard ion chromatographic separations with Biorad™ AG1×8 (0.5 ml of 200-400 mesh) resin were used to purified uranium and thorium. Strontium separates were obtained from the same solutions by piggy-backing separate columns containing 0.25 ml of Sr-Spec™ resin beneath U columns. After initially washing the loaded columns using 7N nitric acid, U and Sr columns were separated and processed independently. The Th cut was eluted from AG1×8 resin using 6N HCl, after which the U was eluted using 0.05N HNO3. Typically, Th required a second cleanup on the same resin, whereas U was sufficiently purified after the first pass. Sr resin was purified by additional washes using 7N HNO3 (about 35 resin volumes in total; De Muynck et al., 2009) followed by elution using 0.05N HNO3.

Purified U salts were loaded on the evaporation side of double-Re-filament assemblies. Thorium salts were loaded on single Re-filament assemblies sandwiched between layers of graphite suspension. Isotope ratios were obtained using a Thermo Finnigan Triton™ thermal ionization mass spectrometer equipped with an RPQ electrostatic filter which reduced abundance sensitivity on a theoretical ^{237}U mass to <5 ppb. Atomic ratios of $^{234}U/^{235}U$, $^{235}U/^{236}U$, $^{230}Th/^{229}Th$, and $^{232}Th/^{229}Th$ were determined using a single ETP™ electron multiplier operating in peak-jumping mode. Sr salts were loaded on single Re center filaments along with a small amount of tantalum-oxide. $^{87}Sr/^{86}Sr$ ratios were collected on the same instrument using faraday cups and a triple-jump multi-dynamic peak-hopping routine.

Raw U and Th data were corrected for mass fractionation using the known $^{236}U/^{233}U$ value in the spike solution for U and a factor of 0.008%/amu for Th, as well as spike contributions, and procedural blanks. Measured $^{234}U/^{235}U$ were converted to $^{234}U/^{238}U$ assuming a $^{238}U/^{235}U$ of 137.88, and were normalized relative to a standard value of 0.0000529 for the $^{234}U/^{238}U$ atomic ratio in NIST SRM 4321B run during the same barrel. Total-process blank contributions varied between 5–10 picograms of uranium and 10–50 picograms of thorium. Corrected ratios were converted to picomole abundances of each isotope and converted to [$^{232}Th/^{238}U$], [$^{230}Th/^{238}U$], and [$^{234}U/^{238}U$] (square brackets used to denote activity ratios) using

values for radioactive decay constants given by Steiger and Jäger (1977) for ^{238}U and ^{232}Th and Cheng et al. (2013) for ^{234}U and ^{230}Th.

Uranium isotopic compositions of the international U-isotope standard, NIST SRM4321B, determined over the same period yielded results within analytical uncertainties of the certified $^{234}U/^{238}U$ value of 0.0000529±0.0000011. Results for a USGS in-house secular equilibrium standard derived from a 69-Ma-old uranium ore from the Schwartzwalder Mine (Ludwig et al. , 1985) yielded results that are analytically indistinguishable from the secular equilibrium value of 1.0000 ([$^{234}U/^{238}U$] = 1.0001 ±0.0033 ±2×standard deviation for N=37, and [$^{230}Th/^{238}U$] = 0.9988±0.0037 ±2×standard deviation for N=31). Analyses of a USGS late Pleistocene *Acropora* coral dating standard (mean age of 119.6 ±1.9 ka for N=17 determined by Watanabe and Nakai, 2006) processed in an identical manner as the unknown samples yielded an average age of 119.4 ±1.2 ka and an initial $^{234}U/^{238}U$ activity ratio of 1.154±0.006 (N=16). All uncertainties presented herein are given at the 95% confidence level (±2σ).

Measurable amounts of common thorium (that is, ^{232}Th) implies that some ^{230}Th not associated with the in-situ decay of parent isotope ^{234}U is present in the sample. To avoid calculating erroneously old $^{230}Th/U$ ages, any initial ^{230}Th derived from detrital sources must be eliminated. This was done mathematically based on the measured [$^{232}Th/^{238}U$], and an assumption about the isotopic composition of the thorium-bearing detrital component (Ludwig and Paces, 2002). The detrital component is assumed to have an atomic Th/U of 4 with the following activity ratios and 2σ errors: [$^{232}Th/^{238}U$] = 1.276±0.64; [$^{234}U/^{238}U$] = 1.0±0.1; and [$^{230}Th/^{238}U$] = 1.0±0.25. Detrital corrected ratios are used to calculate $^{230}Th/U$ ages, initial [$^{234}U/^{238}U$] and associated errors using conventional U-series age equations (Ludwig, 2012).

$^{87}Sr/^{86}Sr$ ratios were normalized for instrumental fractionation using the accepted $^{86}Sr/^{88}Sr$ value of 0.1194. Data for $^{84}Sr/^{86}Sr$ were also collected during the same run to monitor the effectiveness of the fractionation correction. Total-process blank contributions for Sr varied between 100 and 500 picograms.

The mean $^{87}Sr/^{86}Sr$ value obtained for 230 analyses of the NIST international Sr-isotope standard, SRM987, including the period of analysis was 0.710250 ±0.000007 (2×standard deviation), which is within uncertainty of the accepted value of 0.710248±0.000006 (McArthur et al. , 2001). The $^{87}Sr/^{86}Sr$ values determined for unknown samples are normalized to the accepted value using the average value obtained for each batch of analyses. A secondary USGS Sr-isotope standard, EN-1, analyzed as an unknown with each batch, yielded a mean normalized $^{87}Sr/^{86}Sr$ value of 0.709173 ±0.000012 (2×standard deviation for 127 analyses) which is identical to the accepted value of 0.709174±0.000002 (±2×standard error; McArthur et al. , 2006).

Purification and isotope analysis of water samples followed the same procedures as speleothems except that 12 to 157 grams of water were weighed, spiked for U isotope dilution, and evaporated prior processing chemical separations as above. A separate small aliquot of water (~0.5 gram) was spiked with a known amount of ^{84}Sr-enriched tracer solution and run separately to determine Sr concentration by isotope dilution. All determinations of $^{87}Sr/^{86}Sr$ were done on unspiked aliquots.

Table S1. U-Th concentrations, measured and detritus-corrected isotopic compositions, and calculated ^{230}Th/U ages and initial ^{234}U/^{238}U activity ratios for samples of speleothems from Wind Cave National Park.

Sample Name	Sample weight (g)	U conc. (μg/g)	Th conc. (μg/g)	Measured activity ratios[a]							Detritus-corrected activity ratios[b]					^{230}Th/U Age ±2σ (ka)[c]		Initial [^{234}U/^{238}U] ±2σ[c]	
				[^{232}Th/^{238}U]	±2σ	[^{230}Th/ ^{238}U]	±2σ	[^{234}U/ ^{238}U]	±2σ	[^{230}Th/ ^{232}Th]	[^{230}Th/^{238}U]	±2σ	[^{234}U/^{238}U]	±2σ	$\rho_{48\text{-}08}$				
PC01-1	0.0559	2.84	0.013	0.00149	0.00010	1.563	0.007	1.646	0.003	1047	1.563	0.007	1.647	0.003	0.005	217.5	3.0	2.195	0.009
PC02-1	0.0526	3.46	0.013	0.00119	0.00008	1.558	0.007	1.685	0.004	1307	1.558	0.007	1.686	0.004	0.003	201.8	2.7	2.212	0.008
PC02-2	0.0387	1.14	0.094	0.02715	0.00035	1.905	0.012	1.476	0.009	70	1.924	0.016	1.487	0.011	0.290	Excess 230Th		Not calculated	
PC02-3	0.0465	16.86	0.011	0.00022	0.00002	0.139	0.001	2.140	0.005	631	0.139	0.001	2.140	0.005	-0.002	7.27	0.05	2.164	0.005
PC03-1	0.0402	2.55	0.008	0.00105	0.00015	1.529	0.014	1.630	0.004	1450	1.530	0.014	1.630	0.004	0.001	211.8	5.3	2.146	0.017
PC04-1	0.0441	2.49	0.016	0.00207	0.00014	1.565	0.007	1.647	0.005	755	1.566	0.007	1.648	0.005	0.008	217.6	3.1	2.198	0.009
PC05-1	0.0417	4.20	0.009	0.00073	0.00009	1.426	0.006	1.666	0.005	1949	1.427	0.006	1.667	0.005	0.001	170.3	2.0	2.078	0.007
PC05-2	0.0239	3.51	0.010	0.00095	0.00018	1.857	0.010	1.645	0.004	1960	1.858	0.010	1.646	0.004	0.002	437.8	21	3.232	0.127
PC05-3	0.0538	3.37	0.007	0.00072	0.00008	1.560	0.007	1.559	0.004	2158	1.560	0.007	1.559	0.004	0.001	259.8	4.3	2.164	0.012
PC06-1	0.0242	3.00	0.016	0.00175	0.00021	1.486	0.008	1.652	0.007	849	1.487	0.008	1.652	0.007	0.003	190.5	3.0	2.117	0.009
PC06-2	0.0287	2.22	0.003	0.00043	0.00009	1.538	0.008	1.643	0.004	3601	1.538	0.008	1.643	0.004	0.000	209.9	3.3	2.162	0.010
PC06-3	0.0068	3.04	0.007	0.0008	0.00029	1.504	0.010	1.529	0.006	1873	1.504	0.010	1.530	0.006	0.001	248.1	6.2	2.067	0.015
PC07-1	0.0275	4.57	0.008	0.00056	0.00012	1.461	0.006	1.647	0.005	2619	1.461	0.006	1.647	0.005	0.001	184.6	2.2	2.090	0.007
PC07-2	0.0259	2.52	0.006	0.00079	0.00023	1.614	0.007	1.657	0.006	2038	1.614	0.007	1.657	0.006	0.001	232.7	4.0	2.267	0.010
PC07-3	0.0338	2.31	0.008	0.00117	0.00019	1.533	0.007	1.651	0.006	1313	1.534	0.007	1.652	0.006	0.002	205.4	3.0	2.164	0.008
PC07-4	0.0831	3.62	0.008	0.00073	0.00005	1.541	0.006	1.610	0.004	2107	1.541	0.006	1.611	0.004	0.001	224.1	3.1	2.150	0.008
PC08-1	0.0176	3.69	0.382	0.03416	0.00025	1.283	0.007	1.519	0.005	38	1.291	0.011	1.533	0.009	0.298	168.0	3.2	1.856	0.013
PC08-2	0.0307	3.54	0.008	0.00076	0.00014	1.477	0.007	1.639	0.004	1948	1.478	0.007	1.639	0.004	0.001	191.7	2.3	2.098	0.007
PC08-3	0.0446	2.87	0.001	0.00015	0.00005	1.480	0.007	1.646	0.004	9750	1.480	0.007	1.646	0.004	0.000	190.3	2.4	2.106	0.007
PC09C-1	0.2880	3.45	0.002	0.00014	0.00002	1.382	0.006	1.655	0.004	9669	1.382	0.006	1.655	0.004	0.000	162.1	1.5	2.035	0.005
PC10B-1-1	0.0388	3.24	0.100	0.01017	0.00012	1.159	0.005	1.589	0.004	114	1.160	0.005	1.594	0.004	0.064	126.4	1.2	1.849	0.005
PC10B-1-2	0.0208	4.22	0.008	0.00059	0.00017	1.427	0.006	1.626	0.004	2421	1.427	0.006	1.626	0.004	0.001	180.9	2.1	2.043	0.006
PC10B-1-3	0.0243	4.02	0.003	0.00022	0.00015	1.441	0.007	1.676	0.004	6699	1.442	0.007	1.676	0.004	0.000	171.7	2.0	2.098	0.007
PC10B-1-4	0.0279	3.98	0.002	0.00016	0.00014	1.454	0.010	1.679	0.004	8988	1.454	0.010	1.679	0.004	0.000	174.1	2.6	2.111	0.008
PC10B-1-5	0.0375	4.32	0.002	0.00012	0.00009	1.432	0.006	1.640	0.003	12175	1.432	0.006	1.640	0.003	0.000	178.6	1.9	2.059	0.006
PC10B-1-6	0.0489	4.15	0.001	0.00004	0.00007	1.435	0.006	1.633	0.004	32012	1.435	0.006	1.633	0.004	0.000	181.0	1.9	2.056	0.006
PC10B-1-7	0.0476	3.38	0.002	0.00023	0.00009	1.500	0.006	1.657	0.004	6432	1.500	0.006	1.657	0.004	0.000	192.9	2.2	2.133	0.007
PC10B-1-8	0.0484	3.65	0.002	0.0002	0.00009	1.548	0.007	1.620	0.004	7814	1.548	0.007	1.621	0.004	0.000	222.6	3.3	2.163	0.010
PC10B-1-9	0.0336	3.93	0.004	0.0003	0.00011	1.547	0.007	1.602	0.004	5091	1.548	0.007	1.602	0.004	0.000	230.5	3.3	2.154	0.009
PC10B-1-10	0.0344	4.84	0.002	0.00015	0.00009	1.555	0.006	1.602	0.004	10074	1.555	0.006	1.602	0.004	0.000	233.4	3.2	2.164	0.009
PC10B-1-11	0.0573	4.70	0.035	0.00243	0.00006	1.479	0.007	1.511	0.004	609	1.480	0.007	1.512	0.004	0.009	245.9	4.1	2.026	0.010
PC10B-1-12	0.0464	4.93	0.002	0.00014	0.00007	1.411	0.006	1.429	0.004	10354	1.411	0.006	1.429	0.004	0.000	261.8	4.8	1.898	0.010
PC10B-1-13	0.0307	3.65	0.003	0.00025	0.00014	1.501	0.007	1.500	0.005	5889	1.501	0.007	1.500	0.005	0.000	265.8	5.5	2.058	0.013
PC10B-1-14	0.0287	2.50	0.005	0.00059	0.00021	1.495	0.019	1.480	0.004	2530	1.496	0.019	1.481	0.004	0.000	276.8	13.0	2.050	0.037
PC12-1	0.1405	4.67	0.032	0.00224	0.00003	1.420	0.007	1.665	0.004	634	1.421	0.007	1.666	0.004	0.007	169.2	2.1	2.073	0.007
PC13-1	0.1530	4.35	0.020	0.00151	0.00003	1.425	0.007	1.690	0.005	944	1.426	0.007	1.691	0.005	0.003	164.4	2.0	2.099	0.007
PC14-1	0.0302	4.03	0.022	0.00179	0.00012	1.495	0.011	1.694	0.004	835	1.495	0.011	1.695	0.004	0.004	181.0	3.0	2.158	0.010

Sample Name	Sample weight (g)	U conc. (μg/g)	Th conc. (μg/g)	Measured activity ratios[a]							Detritus-corrected activity ratios[b]					^{230}Th/U Age ±2σ (ka)[c]		Initial [^{234}U/^{238}U] ±2σ[c]	
				[^{232}Th/^{238}U] ±2σ		[^{230}Th/ ^{238}U] ±2σ		[^{234}U/ ^{238}U] ±2σ		[^{230}Th/ ^{232}Th]	[^{230}Th/^{238}U] ±2σ		[^{234}U/^{238}U] ±2σ		$\rho_{48\text{-}08}$				
PC14-2	0.0197	5.12	0.007	0.00045	0.00015	1.404	0.008	1.679	0.004	3137	1.404	0.008	1.679	0.004	0.000	161.9	2.0	2.073	0.007
PC15B-1	0.2502	5.62	0.005	0.00028	0.00001	1.410	0.007	1.678	0.004	5041	1.410	0.007	1.678	0.004	0.000	163.7	1.9	2.076	0.006
PC16-1	0.1673	1.97	0.010	0.00176	0.00006	0.008	0.000	1.709	0.018	4	0.006	0.001	1.710	0.018	-0.024	0.40	0.05	1.711	0.018
PC17-1	0.0340	2.25	0.009	0.0013	0.00020	1.269	0.009	1.911	0.004	975	1.269	0.009	1.912	0.005	0.002	106.3	1.3	2.231	0.006
PC17-2	0.0861	2.14	0.003	0.0005	0.00008	1.009	0.005	1.918	0.004	2028	1.009	0.005	1.918	0.004	0.000	76.0	0.5	2.137	0.005
PC17-3	0.0304	2.37	0.016	0.00222	0.00021	1.387	0.010	1.944	0.005	624	1.388	0.010	1.946	0.005	0.006	118.9	1.5	2.323	0.007
PC17-4	0.0296	1.94	0.015	0.00252	0.00026	2.040	0.010	1.905	0.007	810	2.042	0.010	1.907	0.007	0.014	Excess 230Th		Not calculated	
PC17-5	0.0400	2.14	0.014	0.00213	0.00018	0.898	0.005	1.918	0.005	422	0.898	0.005	1.919	0.005	-0.002	65.0	0.6	2.104	0.006
PC17-6	0.0343	2.26	0.027	0.00394	0.00020	1.320	0.009	1.900	0.005	335	1.321	0.009	1.903	0.005	0.017	114.1	1.3	2.246	0.007
PC17-7	0.0413	1.94	0.019	0.0033	0.00019	0.665	0.006	1.922	0.007	202	0.664	0.006	1.925	0.008	-0.012	44.5	0.5	2.049	0.008
PC19-1	0.0199	9.64	0.016	0.00053	0.00008	1.028	0.005	1.824	0.004	1953	1.028	0.005	1.825	0.004	0.000	83.8	0.6	2.045	0.005
PC20-1	0.2567	3.33	0.008	0.00082	0.00002	1.093	0.006	1.992	0.007	1328	1.093	0.006	1.992	0.007	0.000	80.2	0.7	2.245	0.007
PC21-1	0.0456	1.37	0.019	0.00464	0.00024	0.197	0.001	1.802	0.004	42	0.194	0.002	1.804	0.004	-0.229	12.3	0.2	1.833	0.004
PC22A-1	0.0297	4.40	0.011	0.00081	0.00012	1.159	0.005	1.975	0.005	1435	1.160	0.005	1.975	0.005	0.001	88.3	0.7	2.251	0.005
PC22B-1	0.0708	3.24	0.005	0.00046	0.00007	1.062	0.005	1.962	0.005	2297	1.062	0.005	1.963	0.005	0.000	78.8	0.5	2.203	0.005
PC23-1	0.0309	5.05	0.037	0.00238	0.00010	1.121	0.005	1.952	0.004	471	1.121	0.005	1.954	0.005	0.005	85.5	0.6	2.214	0.005
PC24-1	0.1705	3.59	0.003	0.00023	0.00003	1.081	0.004	1.983	0.004	4607	1.081	0.004	1.984	0.004	0.000	79.5	0.5	2.231	0.005
PC26-1	0.0297	0.81	0.010	0.00399	0.00063	1.671	0.010	1.641	0.005	419	1.674	0.010	1.643	0.005	0.021	267.8	6.4	2.369	0.021
PC33A-1	0.0322	2.79	0.102	0.01208	0.00017	1.250	0.009	1.815	0.004	104	1.252	0.009	1.823	0.006	0.088	112.8	1.4	2.132	0.008
PC34-1	0.0349	2.32	0.066	0.0093	0.00019	1.477	0.007	1.884	0.004	159	1.481	0.007	1.890	0.006	0.143	140.1	1.4	2.322	0.007
PC35-1	0.2048	1.90	0.021	0.00363	0.00005	0.068	0.001	1.808	0.006	19	0.065	0.002	1.811	0.006	-0.131	3.99	0.12	1.820	0.006
PC35-2	0.0648	2.87	0.072	0.00824	0.00008	1.492	0.006	1.962	0.004	181	1.495	0.007	1.968	0.005	0.136	132.0	1.2	2.405	0.007
PC37B-1	0.0362	1.83	0.065	0.01161	0.00023	1.774	0.012	1.899	0.005	153	1.781	0.013	1.907	0.006	0.180	199.7	3.5	2.594	0.016
PC39-1	0.0381	2.61	0.054	0.00682	0.00015	1.272	0.006	1.964	0.005	187	1.274	0.006	1.969	0.005	0.056	101.9	0.9	2.292	0.006
PC39-2	0.0403	2.70	0.027	0.00334	0.00014	1.270	0.007	1.958	0.006	380	1.271	0.007	1.960	0.006	0.011	102.2	1.0	2.282	0.007
PC50-1	0.0645	3.22	0.004	0.00042	0.00007	1.461	0.006	1.686	0.004	3510	1.461	0.006	1.686	0.004	0.000	174.2	1.7	2.122	0.006
PC50-2	0.0892	3.39	0.007	0.00067	0.00005	1.440	0.006	1.688	0.004	2135	1.440	0.006	1.688	0.004	0.001	168.6	1.7	2.108	0.006
PC50-3	0.0863	3.07	0.019	0.00203	0.00006	1.522	0.008	1.684	0.004	751	1.523	0.009	1.685	0.004	0.006	191.3	2.8	2.176	0.009
PC51-1	0.0130	21.76	0.048	0.00073	0.00002	0.134	0.001	1.679	0.004	183	0.133	0.001	1.680	0.004	-0.009	8.97	0.10	1.697	0.004
PC51-2	0.0177	12.22	0.141	0.0038	0.00003	0.842	0.004	1.725	0.004	222	0.841	0.004	1.727	0.005	-0.015	69.0	0.5	1.883	0.005
PC51-3	0.0180	3.70	0.026	0.00234	0.00009	1.519	0.015	1.667	0.006	648	1.520	0.015	1.668	0.006	0.003	195.5	5.0	2.160	0.016
PC51-4	0.0237	2.60	0.058	0.00738	0.00010	1.527	0.013	1.511	0.008	207	1.530	0.013	1.514	0.008	0.022	272.9	10	2.111	0.026
PC51-5	0.0130	2.01	0.023	0.00374	0.00023	1.651	0.011	1.489	0.009	442	1.653	0.011	1.490	0.009	0.008	454.1	40	2.77	0.18
PC52-1	0.0877	2.50	0.008	0.00102	0.00007	1.517	0.006	1.688	0.004	1480	1.517	0.006	1.689	0.004	0.002	188.5	2.1	2.173	0.007
PC52-2	0.0940	2.60	0.003	0.00041	0.00006	1.469	0.007	1.685	0.004	3604	1.469	0.007	1.685	0.004	0.000	176.6	2.0	2.128	0.007
PC52-3	0.0527	2.68	0.010	0.00129	0.00011	1.471	0.008	1.678	0.004	1145	1.472	0.008	1.678	0.004	0.003	179.0	2.4	2.124	0.008
BC64-1	0.0109	5.36	0.044	0.00272	0.00026	1.495	0.012	1.979	0.005	549	1.496	0.012	1.981	0.005	0.010	130.5	1.9	2.419	0.009
BC64-2	0.0163	4.56	0.035	0.00252	0.00020	1.103	0.009	1.832	0.004	438	1.103	0.009	1.834	0.004	0.002	92.0	1.1	2.081	0.006

Sample Name	Sample weight (g)	U conc. (μg/g)	Th conc. (μg/g)	Measured activity ratios[a]							Detritus-corrected activity ratios[b]					^{230}Th/U Age ±2σ (ka)[c]		Initial [^{234}U/^{238}U] ±2σ[c]	
				[^{232}Th/^{238}U] ±2σ		[^{230}Th/ ^{238}U] ±2σ		[^{234}U/ ^{238}U] ±2σ		[^{230}Th/ ^{232}Th]	[^{230}Th/^{238}U] ±2σ		[^{234}U/^{238}U] ±2σ		$\rho_{48\text{-}08}$				
BC64-3	0.0141	3.69	0.031	0.00279	0.00029	1.722	0.011	1.683	0.006	617	1.724	0.011	1.684	0.006	0.009	268.9	6.8	2.461	0.023
BC64-4	0.0269	2.92	0.021	0.00235	0.00019	0.755	0.004	1.646	0.004	322	0.754	0.004	1.648	0.004	-0.008	63.8	0.5	1.775	0.005
BC64-5	0.0229	2.91	0.029	0.00329	0.00023	1.082	0.008	1.536	0.007	329	1.082	0.008	1.537	0.007	0.001	120.3	1.8	1.754	0.009
BC70-1	0.0178	0.10	0.009	0.02983	0.00856	3.879	0.038	1.095	0.008	130	3.948	0.057	1.098	0.009	0.109	Excess 230Th		Not calculated	
BC70-2	0.0174	0.40	0.029	0.02416	0.00217	1.486	0.038	1.030	0.007	62	1.496	0.040	1.030	0.008	0.005	Excess 230Th		Not calculated	
BC70-3	0.0300	0.11	0.022	0.06422	0.00461	2.124	0.072	1.093	0.007	33	2.184	0.083	1.098	0.010	0.103	Excess 230Th		Not calculated	
BC70-4	0.0254	0.14	0.008	0.01825	0.00172	1.505	0.016	1.068	0.013	82	1.512	0.017	1.069	0.013	0.008	Excess 230Th		Not calculated	
BC70-5	0.0310	0.19	0.026	0.04487	0.00253	1.583	0.027	1.078	0.005	35	1.604	0.031	1.081	0.006	0.082	Excess 230Th		Not calculated	
BC70-6	0.0370	0.34	0.042	0.041	0.00121	1.965	0.011	1.353	0.006	48	1.997	0.021	1.365	0.009	0.520	Excess 230Th		Not calculated	
BC70-7	0.0237	0.98	0.056	0.01887	0.00065	1.134	0.014	1.711	0.005	60	1.136	0.015	1.722	0.008	0.049	106.5	2.2	1.975	0.010

[a] Measured isotope ratios corrected for mass fractionation, spike contributions, procedural blank and normalized relative to a standard value for NIST SRM 4321b ^{234}U/^{238}U=0.0000529. Activity ratios calculated assuming decay constants of 1.55125×10^{-10} yr^{-1} for ^{238}U, 2.82206×10^{-6} yr^{-1} for ^{234}U, 4.9475×10^{-11} yr^{-1} for ^{232}Th, and 9.1705×10^{-6} yr^{-1} for ^{230}Th (Stieger and Jaeger, 1977; Cheng et al., 2013). Square brackets denote activity ratios.

[b] Assumed Th-bearing detrital component has an atomic Th/U of 4 with the following activity ratios and 2σ errors: [^{232}Th/^{238}U]=1.276±0.64; [^{234}U/^{238}U]=1.0±0.1; and [^{230}Th/^{238}U]=1.0±0.25. Corrections were made to mathematically eliminate detrital ^{230}Th using Isoplot software (Ludwig, 2012). Values for $\rho_{48\text{-}08}$ represents the error correlation between [^{230}Th/^{238}U] and [^{234}U/^{238}U].

[c] ^{230}Th/U age, initial ^{234}U/^{238}U ratio and associated errors calculated using detritus-corrected activity ratios and first-derivative error estimates.

Table S2. Collection dates, locations, and aquifer classifications for water samples near Wind Cave National Park.

Sample Name	Site name	Collection date	Latitude, longitude (in degrees, WGS84)	Hydro-geologic domain[a]	Aquifer[b]
Wind Cave drips					
DP2-150605	Drip site 2	6/5/2015	43.55522, -103.47614	Vadose	Madison
DP3-150605	Drip site 3	6/5/2015	43.55742, -103.47894	Vadose	Madison
PUP-111210	Pile Up	11/12/2010	43.54998, -103.489062	Vadose	Madison
RT66-111210	Route 66	11/12/2010	43.54459, -103.49060	Vadose	Madison
DEEP_140329	Deep End	3/29/2014	43.54099, -103.49079	Vadose	Madison
Cave water bodies					
WTHL-110818	What the Hell Lake	8/18/2011	43.54965, -103.47709	Vadose	Madison
WTHL-120804	What the Hell Lake	8/4/2012	43.54965, -103.47709	Vadose	Madison
WTHL-150605	What the Hell Lake	6/5/2015	43.54965, -103.47709	Vadose	Madison
CL-110818	Calcite Lake	8/18/2011	43.54873, -103.47523	East	Madison
CL-150605	Calcite Lake	6/5/2015	43.54873, -103.47523	East	Madison
VGA-111210	Vega Lake	11/12/2010	43.54162, -103.48934	West	Madison
JwlCv_160214	Jewel Cave Lake	2/14/2016	43.7161, -103.8450	West?	Madison
Artesian springs					
KIDsp-110801	Kidney Spring	8/1/2011	43.434697, -103.481840	Artesian 1	Madison
KIDsp-120805	Kidney Spring	8/5/2012	43.434697, -103.481840	Artesian 1	Madison
HSIsp-110803	Hot Springs Intake Spring	8/3/2011	43.442430, -103.482260	Artesian 1	Madison
HBsp-120805	Hot Brook Spring	8/5/2012	43.451691, -103.509503	Artesian 1	Minnelusa
MNKsp-120805	Minnekahta Spring	8/5/2012	43.434708, -103.485938	Artesian 1	Madison
BCsp-110802	Beaver Creek Spring	8/2/2011	43.524164, -103.375259	Artesian 2	Madison
COOsp-110801	Cool Spring	8/1/2011	43.341162, -103.554852	Artesian 2	Madison
CASsp-110801	Cascade Spring	8/1/2011	43.335290, -103.551726	Artesian 2	Madison
BRsp-120803	Boland Ridge Spring	8/3/2012	43.590357, -103.378968	Artesian 2	Unknown
CBsp-120805	Cold Brook Spring	8/5/2012	43.462248, -103.492702	Artesian 2	Unknown
Shallow springs					
PARsp-120803	Parker Spring	8/3/2012	43.621443, -103.398576	East	White River
HSsp-120805	Horse Shelter Spring	8/5/2012	43.549250, -103.451960	East	Minnelusa
NCsp-120805	Negro Canyon Spring	8/5/2012	43.553595, -103.446436	East	Minnelusa
EMsp-120805	Elk Mountain Spring	8/5/2012	43.559190, -103.488320	West	Minnelusa
WITsp-120806	Witch Spring	8/6/2012	43.566442, -103.603197	West	Minnelusa
WCsp-120805	Woodcock Spring	8/5/2012	43.515169, -103.538458	West	Minnelusa
SLsp-120806	Southerland Spring	8/6/2012	43.672590, -103.583780	Precambrian	Precambrian
RGPsp-120803	Reeves Gulch Pegmatite Spring	8/3/2012	43.599964, -103.489829	Precambrian	Precambrian
Surface flow					
BEVcr-151009	Beaver Creek Sink	10/9/2015	43.584272, -103.459843	Precambrian	Precambrian
HIGHcr-120803	Highland Creek sink	8/3/2012	43.629297, -103.439094	Precambrian	Precambrian
FRcr-120806	Falls River Creek at the falls	8/6/2012	43.401776, -103.410402	Artesian 1	Madison

[a] Hydrologic domain based on results of principal component and cluster analyses of Long et al. (2012, Table 2), except for Highland Creek sink and Beaver Creek sink, which were classified on the basis of elevated Sr isotopic compositions, and Vega and Jewel Cave lakes which were not included in earlier studies.

[b] Aquifer classification is from Long et al. (2012).

References

Cheng, H., Edwards, R.L., et al., 2013, Improvements in ^{230}Th dating, ^{230}Th and ^{234}U half-life values, and U–Th isotopic measurements by multi-collector inductively coupled plasma mass spectrometry: Earth and Planetary Science Letters, v. 371–372, p. 82–91, https://doi.org/10.1016/j.epsl.2013.04.006.

De Muynck, D. Huelga-Suarez, G., Van Heghe, L., Degryse, P., and Vanhaecke, F., 2009, Systematic evaluation of a strontium-specific extraction chromatographic resin for obtaining a purified Sr fraction with quantitative recovery from complex and Ca-rich matrices: Journal of Analytical Atomic Spectrometry, v. 24, p. 1498–1510, doi:10.1039/B908645E.

Ludwig, K.R., 2012, User's manual for Isoplot 3.75, A geochronological toolkit for Microsoft Excel: Berkeley Geochronological Center Special Publication No. 5, 75 p., http://bgc.org/isoplot_etc/isoplot/Isoplot3_75-4_15manual.pdf.

Ludwig, K.R., Wallace, A.R., and Simmons, K.R., 1985, The Schwartzwalder uranium deposit, II: age of uranium mineralization and Pb-isotope constraints on genesis: Economic Geology, v. 80, p. 1858–1871, https://doi.org/10.2113/gsecongeo.80.7.1858.

Ludwig, K.R., and Paces, J.B., 2002, Uranium-series dating of pedogenic silica and carbonate, Crater Flat, Nevada: Geochimica et Cosmochimica Acta, v. 66, p. 487–506, https://doi.org/10.1016/S0016-7037(01)00786-4.

McArthur, J.M, Howarth, R.J., and Bailey, R.R., 2001, Strontium isotope stratigraphy: LOWESS version 3: best fit to the marine Sr-isotope curve for 0–509 Ma and accompanying look-up table for deriving numerical age: Journal of Geology, v. 109, p. 155–170, https://doi.org/10.1086/319243.

McArthur, J.M., Rio, D., Massari, F., Castradori, D., Bailey, T.R., Thirlwall, M., and Houghton, S., 2006, A revised Pleocene record for marine-^{87}Sr/^{86}Sr used to date an interglacial event recorded in the Cockburn Island Formation, Antarctic Peninsula: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 242, p. 126-136, https://doi.org/10.1016/j.palaeo.2006.06.004.

Steiger, R.H., and Jäger, E., 1977, Subcommission on geochronology: convention on the use of decay constants in geo- and cosmochronology: Earth and Planetary Science Letters, v. 36, p. 359–362, https://doi.org/10.1016/0012-821X(77)90060-7.

Watanabe, Yumiko, and Nakai, Shun'ichi, 2006, U-Th radioactive disequilibrium analyses for JCp-1, coral reference distributed by the Geological Survey of Japan: Geochemical Journal, v. 40, p. 537-541, https://doi.org/10.2343/geochemj.40.537.