Polyak et al., 2017, Rapid speleothem δ^{13}C change in southwestern North America coincident with Greenland stadial 20 and the Toba (Indonesia) supereruption: Geology, doi:10.1130/G39149.1.
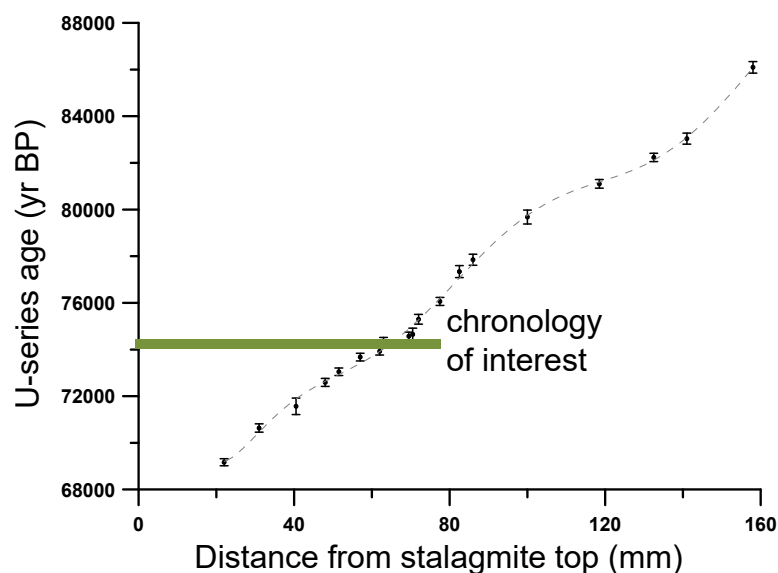

METHODS

Uranium (U)-series. U-series isotope measurements were made at the Radiogenic Isotope Laboratory, University of New Mexico. Subsample powders (100 to 170 mg) were drilled and dissolved in concentrated nitric acid, and then spiked with a mixed solution of ^{229}Th-^{233}U-^{236}U. U and Th were separated using conventional anion-exchange chromatography (Asmerom et al., 2010). U and Th measurements were made on a Thermo Neptune multicollector inductively coupled plasma mass spectrometer (MC-ICPMS). The MC-ICPMS measurements were run in static mode using a mix of 10^{11} and 10^{12} Ω resistors in conjunction with five Faraday cup detectors and an ion-counting secondary electron multiplier detector. A NBL-112 II (also known as CRM-145) U isotope standard was measured with the samples, yielding a δ^{234}U value of −38.0. U and Th procedural blanks were in the range of 5–10 pg and therefore have no effect on ages. The analytical uncertainties are 2σ of the mean. The age uncertainties include analytical errors and uncertainties in the initial ^{230}Th/^{232}Th ratios. Initial ^{230}Th/^{232}Th ratios were corrected using an empirical value of 30 ±15 ppm, allowing for a range of contributions, from silicate to carbonate materials. The sample is very clean and thus not sensitive to initial ^{230}Th correction, in addition to the fact that the samples are older than 10 kyrs. The sample and U-series growth curve are shown in Figure DR1.
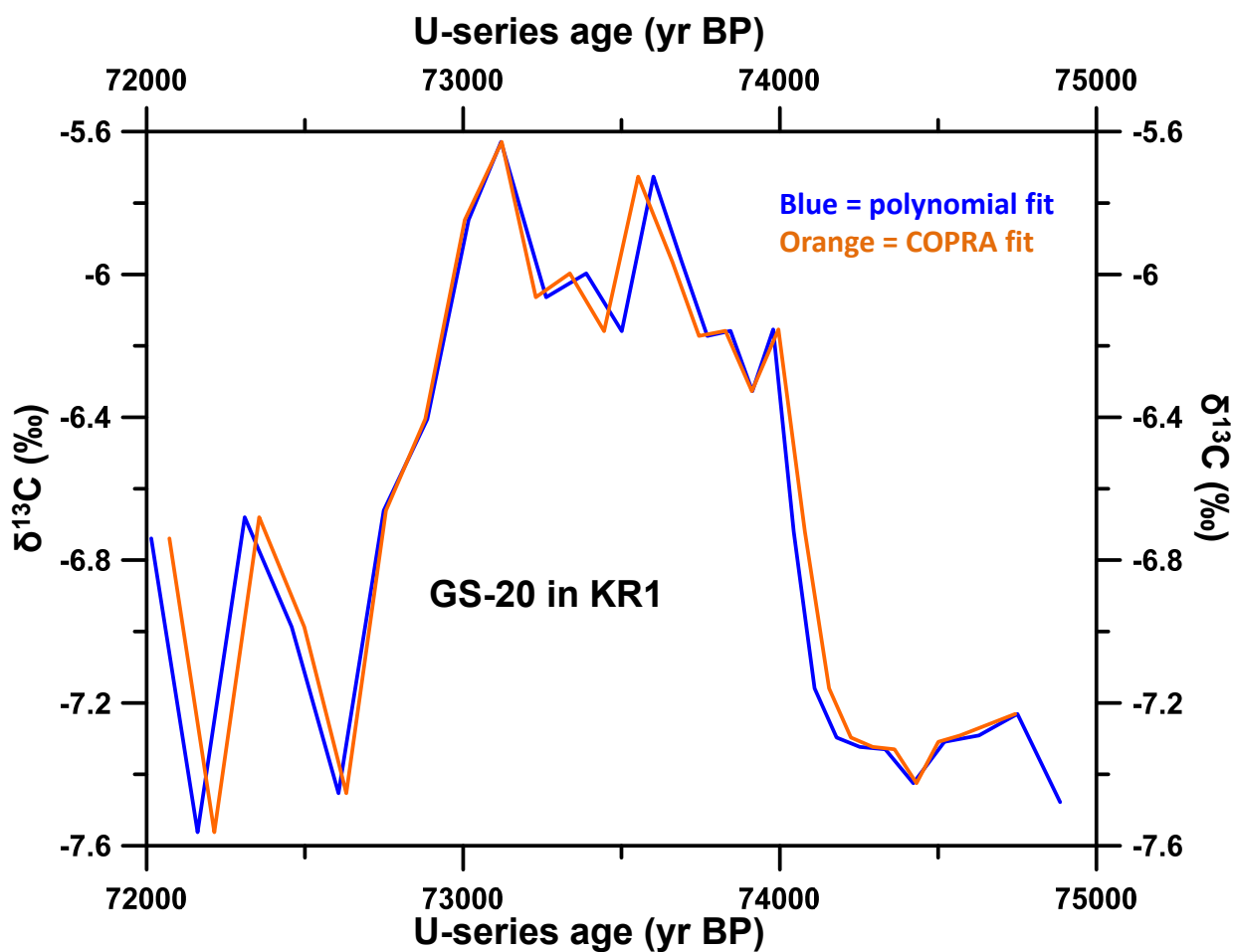
Stable isotopes. Powders for δ^{18}O analysis were sampled along the stalagmite growth axis at 1 mm intervals and were analyzed at the Las Vegas Isotope Science Lab (LVIS) of the University of Nevada, Las Vegas. Stalagmite powders were reacted with three drops of anhydrous phosphoric acid at 70 °C in a Thermo Electron Kiel-IV automated carbonate preparation device coupled to a Delta V Plus mass spectrometer. Values are reported in standard permil (‰) notation with respect to Vienna Pee Dee Belemnite (VPDB). Internal standard precision is better than 0.08 ‰ δ^{18}O.

Subsampling for U-series. Sample trenches were milled using a 1 mm diameter bit with resultant trench widths of 1.2 mm. The growth rate of KR-1 through this region of the stalagmite is 0.0075 mm/yr (133 years/mm). An additional maximum error equal to half of the trench width (0.6 mm) is 80 years, was added to the U-series error (191 + 80 = 271 years) for the age measured at the initiation of GS-20. We interpret the timing of rapid rise in δ^{13}C to be 74190 ± 220 yr B.P. COPRA was used to construct the age model. An age model using multiple polynomial curves was also constructed and both curves compared well (Figure DR2).

Figure DR1. Stalagmite KR-1 consists mostly of pre-penultimate glacial growth with the most recent growth branching from the main part of the stalagmite as shown in this figure. Except for the top 22 mm (hiatus shown in gold), this part of the stalagmite grew from 87 to 69 ka, and the uranium-series chronology supports continuous growth through this section of the stalagmite. Sample trenches are 1.2 mm wide and drilled along growth layers. Circles are added sample sites for $\delta^{234}U$ measurements.

The graph below shows the uranium-series chronology tied to distance below stalagmite top, and exhibits the growth rate character of the stalagmite, which is near linear around the Toba super-eruption time.

chronology of interest

Figure DR2. Comparison of polynomial and COPRA curves. The polynomial curve is constructed of three polynomial equations. Both curves produce a suitable age model.

Table DR1. Uranium-series results for stalagmite KR1.

dist. (mm)	^{238}U (ng/g)	^{232}Th (pg/g)	$^{230}Th/^{232}Th$ act. ratio	$^{230}Th/^{238}U$ act. ratio	measured $\delta^{234}U$ (‰)	initial $\delta^{234}U$ (‰)	uncorrected age (yr BP)	corrected age (yrs BP)
7	129.7 ± 0.1	51 ± 37	3107 ± 2256	0.403 ± 0.001	1160 ± 2	1235 ± 2	22119 ± 73	**22114 ± 73**
13.5	162.1 ± 0.1	64 ± 83	3866 ± 5011	0.500 ± 0.002	1128 ± 2	1222 ± 2	28553 ± 144	**28548 ± 144**
22	494.5 ± 0.4	68 ± 32	19947 ± 9309	0.893 ± 0.001	825 ± 2	1003 ± 2	69167 ± 150	**69165 ± 150**
31	141.1 ± 0.1	27 ± 43	15582 ± 25360	0.961 ± 0.002	928 ± 2	1133 ± 2	70634 ± 178	**70635 ± 178**
40.5	396.5 ± 0.2	0 ± 41	3442266 ± 425147589	0.933 ± 0.003	856 ± 2	1047 ± 3	71566 ± 356	**71566 ± 356**
48	513.2 ± 0.5	108 ± 43	13031 ± 5234	0.897 ± 0.001	769 ± 2	944 ± 2	72593 ± 174	**72590 ± 174**
51.5	432.6 ± 0.3	8 ± 45	148852 ± 800384	0.950 ± 0.001	862 ± 2	1059 ± 2	73046 ± 161	**73046 ± 161**
57	279.9 ± 0.2	14 ± 42	57672 ± 169322	0.954 ± 0.001	858 ± 2	1057 ± 2	73676 ± 164	**73676 ± 164**
62	335.8 ± 0.2	84 ± 38	11348 ± 5168	0.934 ± 0.001	816 ± 2	1006 ± 2	73926 ± 158	**73922 ± 158**
63	341.4 ± 0.4	0 ± 41	35796 ± 52404	0.942 ± 0.002	825 ± 2	1018 ± 2	74304 ± 214	**74303 ± 214**
69.5	309.5 ± 0.2	22 ± 45	39776 ± 79353	0.945 ± 0.001	826 ± 2	1019 ± 2	74568 ± 176	**74567 ± 176**
70.5	252.9 ± 0.2	67 ± 95	10841 ± 15299	0.945 ± 0.002	824 ± 2	1017 ± 2	74655 ± 265	**74651 ± 265**
72	413.1 ± 0.3	90 ± 58	13388 ± 8622	0.949 ± 0.002	821 ± 2	1015 ± 2	75301 ± 209	**75298 ± 209**
77.5	393.7 ± 0.2	72 ± 45	15740 ± 9807	0.946 ± 0.001	802 ± 2	994 ± 2	76062 ± 173	**76060 ± 173**
82.5	392.3 ± 0.2	85 ± 42	13305 ± 6506	0.945 ± 0.002	779 ± 2	969 ± 2	77343 ± 256	**77340 ± 256**
86	210.2 ± 0.2	258 ± 35	2504 ± 344	1.005 ± 0.002	877 ± 2	1093 ± 2	77868 ± 236	**77851 ± 236**
100	241.8 ± 0.1	33 ± 58	22225 ± 38759	1.008 ± 0.003	853 ± 2	1068 ± 2	79682 ± 299	**79680 ± 299**
118.5	240.0 ± 0.1	31 ± 51	23791 ± 38526	1.021 ± 0.001	854 ± 2	1073 ± 2	81101 ± 186	**81099 ± 186**
132.5	296.3 ± 0.1	29 ± 28	31991 ± 31084	1.031 ± 0.001	853 ± 2	1076 ± 2	82235 ± 178	**82234 ± 178**
141	319.3 ± 0.2	195 ± 45	6863 ± 1983	1.034 ± 0.002	846 ± 2	1069 ± 2	83043 ± 236	**83037 ± 236**
158	298.3 ± 0.3	27 ± 38	36316 ± 52024	1.060 ± 0.002	844 ± 2	1077 ± 2	86096 ± 246	**86095 ± 246**
111	335.1 ± 0.2	195 ± 45	5368 ± 1238	1.025 ± 0.002	853 ± 2	1074 ± 2	81581 ± 213	**81573 ± 213**

dist. (mm)	Age from age model (yr BP)	initial $\delta^{234}U$ (‰)
26	70045	1040 ± 5
32	70731	1092 ± 5
34	70896	1048 ± 4
36	71067	1079 ± 5
39	71367	1079 ± 6
42.5	71804	984 ± 4
45	72161	1040 ± 4
60	73913	1022 ± 6
62	73922	992 ± 6
66	74333	1004 ± 3
69.5	74567	1019 ± 2
80	76706	988 ± 5
85	77668	1046 ± 7
90	78449	1039 ± 6
96	79236	1064 ± 5
99.5	79625	1044 ± 6

Yr BP = years before 2000 AD. All errors are absolute 2-σ. An additional error of 80 years (1/2 the trench width equivalent) has been added to the measured errors shown in this table. The age data with larger errors were used in COPRA to produce the final age model. For example, an error of 294 years for the date at 63 mm of 74303 ± 214 was used for the COPRA reduction of data. Dist. = distance in mm from stalagmite top. There are growth hiatuses at 22 and 168 mm below the stalagmite top. Subsample 111 was rejected due to milling inaccuracy (see Figure DR1).

Additional $\delta^{234}U$ values were measured from small powders (~20 mg). Ages for these were assigned from our age model using distances.

Table DR2. Oxygen and carbon stable isotope values for stalagmite KR1.

dist.	Age (yr BP, calc.)	δ¹³C (‰)	dist.	Age (yr BP, calc.)	δ¹³C (‰)	dist.	Age (yr BP, calc.)	δ¹³C (‰)
23	69324 ± 205	-7.04	68	74500 ± 198	-7.31	113	80680 ± 199	-7.98
24	69486 ± 186	-7.22	69	74569 ± 217	-7.29	114	80757 ± 207	-8.09
25	69648 ± 172	-6.84	70	74744 ± 194	-7.23	115	80833 ± 217	-8.30
26	69811 ± 166	-6.95	71	75023 ± 189	-7.48	116	80910 ± 228	-8.08
27	69973 ± 167	-6.85	72	75302 ± 265	-7.55	117	80987 ± 240	-7.99
28	70135 ± 176	-6.60	73	75440 ± 222	-7.52	118	81063 ± 254	-8.57
29	70297 ± 192	-6.57	74	75579 ± 192	-7.36	119	81142 ± 251	-8.04
30	70459 ± 213	-6.15	75	75717 ± 181	-7.45	120	81222 ± 234	-7.64
31	70621 ± 238	-5.85	76	75855 ± 192	-7.35	121	81302 ± 218	-7.23
32	70722 ± 218	-6.09	77	75994 ± 222	-7.14	122	81382 ± 205	-7.82
33	70822 ± 207	-6.31	78	76186 ± 220	-7.41	123	81462 ± 194	-7.76
34	70923 ± 208	-6.86	79	76432 ± 192	-7.36	124	81542 ± 186	-8.12
35	71023 ± 218	-6.62	80	76677 ± 192	-7.35	125	81623 ± 181	-8.28
36	71123 ± 239	-6.99	81	76923 ± 222	-7.37	126	81703 ± 180	-8.56
37	71224 ± 266	-6.61	82	77169 ± 271	-7.59	127	81783 ± 183	-8.35
38	71324 ± 298	-6.71	83	77380 ± 268	-7.12	128	81863 ± 189	-9.11
39	71424 ± 334	-6.95	84	77556 ± 231	-7.07	129	81943 ± 198	-8.60
40	71525 ± 373	-6.87	85	77733 ± 239	-7.17	130	82023 ± 210	-8.00
41	71646 ± 366	-7.14	86	77909 ± 289	-7.34	131	82104 ± 224	-8.31
42	71788 ± 316	-6.77	87	78036 ± 270	-7.42	132	82184 ± 241	-8.11
43	71930 ± 270	-7.97	88	78163 ± 251	-7.36	133	82272 ± 236	-8.07
44	72072 ± 233	-6.74	89	78290 ± 234	-7.85	134	82369 ± 215	-7.91
45	72214 ± 210	-7.56	90	78416 ± 220	-7.51	135	82466 ± 202	-7.72
46	72356 ± 204	-6.68	91	78543 ± 208	-7.61	136	82563 ± 199	-7.99
47	72498 ± 218	-6.99	92	78670 ± 200	-7.69	137	82660 ± 207	-8.08
48	72631 ± 208	-7.45	93	78797 ± 195	-7.56	138	82757 ± 224	-7.93
49	72756 ± 176	-6.66	94	78924 ± 193	-7.68	139	82854 ± 248	-7.94
50	72881 ± 169	-6.41	95	79051 ± 196	-7.57	140	82951 ± 278	-7.90
51	73005 ± 189	-5.85	96	79177 ± 203	-7.44	141	83048 ± 312	-7.87
52	73121 ± 191	-5.63	97	79304 ± 213	-7.59	142	83227 ± 294	-7.84
53	73229 ± 165	-6.06	98	79431 ± 225	-7.63	143	83407 ± 278	-8.25
54	73337 ± 154	-6.00	99	79558 ± 241	-7.85	144	83586 ± 263	-8.15
55	73445 ± 161	-6.16	100	79685 ± 258	-7.88	145	83765 ± 250	-7.90
56	73553 ± 183	-5.73	101	79761 ± 245	-8.13	146	83944 ± 239	-7.89
57	73661 ± 215	-5.97	102	79838 ± 232	-8.02	147	84123 ± 232	-7.96
58	73744 ± 190	-6.17	103	79914 ± 220	-8.15	148	84302 ± 227	-7.95
59	73828 ± 177	-6.16	104	79991 ± 210	-8.25	149	84481 ± 225	-7.65
60	73912 ± 178	-6.33	105	80068 ± 201	-8.00	150	84660 ± 227	-7.68
61	73995 ± 193	-6.15	106	80144 ± 194	-8.02	151	84840 ± 232	-7.75
62	74079 ± 220	-6.72	107	80221 ± 189	-8.08	152	85019 ± 239	-7.05
63	74155 ± 224	-7.16	108	80297 ± 185	-7.78	153	85198 ± 250	-7.46
64	74224 ± 203	-7.30	109	80374 ± 184	-7.96	154	85377 ± 263	-7.26
65	74293 ± 190	-7.32	110	80451 ± 184	-7.86	155	85556 ± 278	-7.64
66	74362 ± 184	-7.33	111	80527 ± 187	-7.74	156	85735 ± 294	-7.64
67	74431 ± 187	-7.43	112	80604 ± 192	-7.86	157	85914 ± 312	-7.45
						158	86094 ± 332	-7.80

Dist. = distance in mm beneath the stalagmite top. An age is calculated by COPRA for each subsample δ¹³C value, and errors are generated at 95% confidence level for the calculated ages. The U-series ages that were input into COPRA had associated 2-σ absolute errors, and 80 years to account for sampling error was added to those.

Table DR2. Oxygen and carbon stable isotope values for stalagmite KR1, continued.

dist.	Age (yr BP, calc.)	δ¹⁸O (‰)	dist.	Age (yr BP, calc.)	δ¹⁸O (‰)	dist.	Age (yr BP, calc.)	δ¹⁸O (‰)
23	69328 ± 134	-8.65	68	74479 ± 142	-7.84	113	80679 ± 142	0.14
24	69490 ± 122	-8.41	69	74546 ± 159	-7.52	114	80756 ± 148	0.16
25	69652 ± 115	-8.57	70	74723 ± 142	-8.00	115	80833 ± 156	0.18
26	69814 ± 113	-7.68	71	75011 ± 140	-7.63	116	80910 ± 164	0.19
27	69976 ± 117	-8.64	72	75299 ± 204	-7.76	117	80987 ± 173	0.21
28	70138 ± 126	-8.68	73	75438 ± 169	-7.67	118	81065 ± 183	0.24
29	70299 ± 140	-8.77	74	75577 ± 143	-7.80	119	81143 ± 181	0.27
30	70461 ± 156	-8.16	75	75717 ± 131	-7.42	120	81224 ± 167	0.29
31	70623 ± 175	-8.54	76	75856 ± 136	-7.68	121	81304 ± 155	0.27
32	70723 ± 163	-8.45	77	75995 ± 158	-7.70	122	81384 ± 144	0.23
33	70824 ± 159	-8.29	78	76189 ± 158	-7.73	123	81465 ± 135	0.22
34	70924 ± 165	-8.55	79	76438 ± 143	-7.85	124	81545 ± 128	0.20
35	71024 ± 180	-8.41	80	76687 ± 151	-7.46	125	81626 ± 123	0.16
36	71124 ± 201	-8.34	81	76935 ± 179	-7.69	126	81706 ± 121	0.12
37	71224 ± 228	-8.44	82	77184 ± 219	-7.59	127	81786 ± 122	0.11
38	71324 ± 257	-8.48	83	77389 ± 214	-7.59	128	81867 ± 126	0.12
39	71425 ± 290	-8.64	84	77552 ± 179	-7.61	129	81947 ± 132	0.14
40	71525 ± 323	-8.54	85	77714 ± 184	-7.46	130	82027 ± 141	0.15
41	71647 ± 316	-8.23	86	77876 ± 226	-7.42	131	82108 ± 151	0.14
42	71792 ± 269	-8.27	87	78004 ± 210	-7.62	132	82188 ± 163	0.13
43	71936 ± 225	-8.07	88	78133 ± 195	-7.25	133	82276 ± 160	0.13
44	72081 ± 188	-8.36	89	78262 ± 181	-7.40	134	82372 ± 146	0.13
45	72225 ± 160	-8.10	90	78390 ± 169	-7.56	135	82468 ± 138	0.17
46	72370 ± 148	-8.44	91	78519 ± 158	-7.46	136	82564 ± 139	0.22
47	72515 ± 155	-8.29	92	78647 ± 149	-7.31	137	82660 ± 148	0.26
48	72645 ± 147	-8.28	93	78776 ± 142	-7.05	138	82756 ± 164	0.23
49	72761 ± 123	-8.44	94	78904 ± 139	-7.06	139	82852 ± 185	0.19
50	72877 ± 121	-8.03	95	79033 ± 138	-6.87	140	82948 ± 210	0.16
51	72993 ± 142	-8.27	96	79161 ± 140	-6.85	141	83044 ± 237	0.15
52	73107 ± 145	-8.12	97	79290 ± 145	-6.65	142	83223 ± 223	0.14
53	73218 ± 123	-8.11	98	79419 ± 153	-7.05	143	83403 ± 210	0.11
54	73329 ± 113	-8.28	99	79547 ± 163	-6.93	144	83582 ± 198	0.11
55	73440 ± 117	-8.28	100	79676 ± 175	-7.16	145	83762 ± 188	0.13
56	73551 ± 134	-8.43	101	79753 ± 166	-7.09	146	83941 ± 180	0.15
57	73663 ± 160	-8.31	102	79830 ± 158	-7.12	147	84121 ± 173	0.16
58	73744 ± 138	-8.29	103	79907 ± 150	-6.71	148	84300 ± 169	0.15
59	73826 ± 127	-8.57	104	79984 ± 143	-6.81	149	84480 ± 167	0.09
60	73908 ± 130	-8.33	105	80062 ± 137	-6.94	150	84659 ± 168	0.10
61	73990 ± 146	-8.19	106	80139 ± 133	-6.56	151	84839 ± 171	0.18
62	74071 ± 170	-8.14	107	80216 ± 130	-6.96	152	85018 ± 177	0.19
63	74146 ± 173	-7.75	108	80293 ± 128	-6.91	153	85198 ± 184	0.12
64	74212 ± 153	-8.17	109	80370 ± 128	-6.57	154	85377 ± 194	0.09
65	74279 ± 138	-7.97	110	80447 ± 129	-7.04	155	85556 ± 205	0.11
66	74346 ± 131	-7.97	111	80524 ± 132	-6.97	156	85736 ± 217	0.11
67	74413 ± 132	-7.50	112	80602 ± 136	-6.70	157	85915 ± 231	0.12
						158	86095 ± 246	0.11

Dist. = distance in mm beneath the stalagmite top. An age is calculated by COPRA for each subsample δ¹⁸O value, and errors are generated at 95% confidence level for the calculated ages. The U-series ages that were input into COPRA had associated 2-σ absolute errors, and 80 years to account for sampling error was added to those.