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Last glacial millennial-scale hydro-climate and temperature changes in Puerto Rico constrained by speleothem fluid inclusion δ^{18}O and δ^{2}H values

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S.1 Supplementary tables

Table S1: Results for fluid inclusion samples analysed different distances from top (dft) including released water volume, water content and measured stable isotope composition δ^{18}O and δ^{2}H (in ‰ VSMOW) of each sample at the respective depths. Single measurements marked with (*) are not taken into account for paleo-temperature calculation due to released water volume of <0.2 µl or poor reproducibility (see text for more details).

Sample ID	dft (total)	dft (Error)	sample volume	water content	δ^{18}O	δ^{18}O (Error)	δ^{2}H	δ^{2}H (Error)
	[mm]	[mm]	[µl]	[µl/g]	[‰]	[‰]	[‰]	[‰]
1_A	9.00	3.00	0.33	0.66	1.95	0.50	34.39	1.50
1_B*	9.00	3.00	0.28	0.67	3.97	0.50	32.32	1.50
5_A*	32.00	2.00	0.11	0.31	8.95	0.50	37.26	1.50
5_B*	32.00	2.00	0.14	0.30	6.25	0.50	41.57	1.50
5b_A	38.00	2.00	0.45	0.42	0.88	0.50	24.00	1.50
5b_B	38.00	2.00	0.37	0.36	-1.32	0.50	16.91	1.50
7_A*	112.75	0.75	0.04	0.12	10.77	0.50	39.40	1.50
7_B*	112.75	0.75	0.02	0.08	12.03	0.50	42.96	1.50
7b_A	160.00	2.00	0.47	0.64	-0.71	0.50	11.20	1.50
7b_B*	160.00	2.00	2.98	2.21	4.68	0.50	19.34	1.50
8_A	212.00	2.00	0.20	0.57	-1.38	0.50	16.07	1.50
8_B	212.00	2.00	0.29	0.48	-2.07	0.50	20.99	1.50
9a_A*	293.00	1.50	0.10	0.31	4.81	0.50	18.81	1.50
9a_B*	293.00	1.50	0.11	0.45	3.25	0.50	15.89	1.50
9b_A*	291.50	1.50	0.22	0.54	1.70	0.50	13.18	1.50
9b_B	301.00	4.00	0.18	0.85	0.25	0.50	7.34	1.50
9c_A*	301.00	4.00	0.46	0.66	1.27	0.50	12.37	1.50
9c_B*	301.00	4.00	0.65	0.84	2.41	0.50	12.52	1.50
10_A	370.00	1.00	0.78	1.81	-0.21	0.50	6.81	1.50
10_B	370.00	1.00	0.60	1.56	-0.64	0.50	8.39	1.50
10_C	370.00	1.00	0.70	2.21	-0.88	0.50	5.90	1.50
12_A	482.50	2.50	0.34	0.71	1.02	0.50	13.29	1.50
12_B*	482.50	2.50	0.44	0.71	1.67	0.50	11.53	1.50
13_A	525.00	2.50	0.72	1.27	-2.64	0.50	6.38	1.50
13_B	525.00	2.50	1.06	2.07	-0.99	0.50	7.08	1.50
13_C	525.00	2.50	1.34	2.70	-1.98	0.50	7.10	1.50
14_A*	642.00	2.00	0.16	0.47	3.61	0.50	20.96	1.50
14_B*	642.00	2.00	0.08	0.35	2.25	0.50	19.76	1.50
15_A	689.50	19.50	0.84	1.49	-0.37	0.50	13.15	1.50
15_B*	667.50	2.50	0.17	0.33	1.52	0.50	19.80	1.50
15b_A*	689.50	19.50	0.26	0.62	1.60	0.50	12.67	1.50
15b_B	689.50	19.50	1.15	1.53	-0.81	0.50	11.27	1.50
15b_C	694.50	2.50	0.17	0.50	-0.78	0.50	20.41	1.50

15c_A	689.50	19.50	0.99	1.39	-0.04	0.50	12.47	1.50
15c_B	689.50	19.50	0.65	0.88	-0.40	0.50	17.18	1.50
16_A	745.00	2.00	0.74	3.05	0.02	0.50	10.59	1.50
16_B	745.00	2.00	0.93	2.83	-0.14	0.50	10.41	1.50
17_A*	827.50	1.50	0.12	0.27	5.15	0.50	30.45	1.50
17_B*	827.50	1.50	0.34	0.52	1.64	0.50	23.11	1.50
17b_A*	831.50	3.50	0.23	0.38	8.04	0.50	27.88	1.50
17b_B*	831.50	3.50	0.25	0.40	4.83	0.50	27.10	1.50
18_A	940.00	2.50	0.24	0.53	0.65	0.50	23.25	1.50
18_B*	940.00	2.50	0.14	0.45	2.98	0.50	27.29	1.50
18_C	940.00	2.50	0.29	0.77	1.20	0.50	18.26	1.50
19_A	1010.50	11.50	0.25	0.44	0.59	0.50	20.26	1.50
19_B	1010.50	11.50	0.43	0.74	-0.96	0.50	17.19	1.50
20_A	1010.50	11.50	1.21	2.24	-0.71	0.50	12.43	1.50
21b_A	1028.00	3.00	1.19	1.74	0.44	0.50	14.67	1.50
21b_B*	1028.00	3.00	0.39	0.53	4.43	0.50	22.73	1.50
22_A*	1045.50	1.50	0.08	0.18	8.21	0.50	43.40	1.50
22_B*	1045.50	1.50	0.07	0.15	8.28	0.50	37.87	1.50
23_A*	1052.00	2.00	0.17	0.55	3.50	0.50	25.21	1.50
23_B*	1052.00	2.00	0.13	0.53	3.30	0.50	25.75	1.50
24_A	1079.50	9.50	0.29	0.48	0.03	0.50	20.17	1.50
24_B	1079.50	9.50	0.22	0.39	0.64	0.50	30.49	1.50
24b_A*	1082.00	2.00	0.32	0.40	7.85	0.50	28.91	1.50
24b_B*	1082.00	2.00	0.06	0.08	11.27	0.50	33.31	1.50
24c_A	1079.50	9.50	0.83	1.30	0.53	0.50	14.53	1.50
24c_B	1079.50	9.50	0.76	1.10	-1.12	0.50	9.99	1.50
24c_C*	1088.00	2.00	0.24	0.48	10.74	0.50	35.12	1.50
25_A*	1235.00	1.50	0.12	0.27	9.29	0.50	47.60	1.50
25_B*	1235.00	1.50	0.27	0.42	4.68	0.50	27.75	1.50
27_A	1398.00	10.00	0.27	0.79	0.94	0.50	14.55	1.50
27_B	1398.00	10.00	0.27	0.38	-0.40	0.50	18.05	1.50
27b_A*	1407.00	3.00	0.20	0.37	2.13	0.50	19.65	1.50
27b_B*	1398.00	10.00	0.69	0.57	1.39	0.50	17.81	1.50
28_A	1441.00	2.00	0.58	1.21	0.16	0.50	15.53	1.50
28_B	1441.00	2.00	0.56	1.50	0.36	0.50	12.66	1.50
28_C	1441.00	2.00	1.11	2.24	0.09	0.50	12.49	1.50
30_A*	1463.00	2.00	0.18	0.36	11.88	0.50	45.26	1.50
30_B*	1463.00	2.00	0.11	0.24	8.83	0.50	44.63	1.50
31_A*	1504.50	2.50	0.12	0.42	4.04	0.50	25.07	1.50
31_B*	1504.50	2.50	0.37	0.50	5.61	0.50	29.62	1.50
32_A	1554.50	2.50	0.15	0.35	0.74	0.50	18.60	1.50
32_B	1554.50	2.50	0.31	0.55	0.81	0.50	20.03	1.50
32b_A*	1556.00	4.50	0.93	1.22	8.59	0.50	25.74	1.50
32b_B*	1556.00	4.50	0.50	0.82	8.35	0.50	28.68	1.50
32b_C*	1556.00	4.50	0.26	0.37	4.75	0.50	20.67	1.50
33_A	1637.50	2.50	0.18	0.47	0.36	0.50	10.61	1.50
33_B*	1637.50	2.50	0.22	0.30	6.19	0.50	22.94	1.50

34_A*	1725.00	2.00	0.32	0.68	13.48	0.50	28.18	1.50
34_B*	1725.00	2.00	0.37	0.46	2.67	0.50	23.45	1.50
34b_A*	1742.50	4.50	1.19	1.57	9.69	0.50	27.12	1.50
34b_B*	1742.50	4.50	0.66	0.92	3.73	0.50	18.67	1.50
35_A	1767.50	1.50	0.63	1.83	1.00	0.50	16.97	1.50
35_B	1767.50	1.50	0.58	1.84	0.17	0.50	17.27	1.50
35_C	1767.50	1.50	0.32	1.04	1.66	0.50	20.48	1.50
36_A	1819.50	3.50	0.25	0.60	-0.53	0.50	14.63	1.50
36_B*	1819.50	3.50	0.30	0.54	3.56	0.50	17.73	1.50

Table S2: Resume of stable isotope data and calculated paleo-temperatures from the mean values of replicate measurements, including the mean water content and measured stable isotope composition $\delta^{18}O_f$ and $\delta^{2}H_f$ (in ‰ VSMOW). The age and associated uncertainty for the individual depths integrated by each sample was calculated using the age model of Warken et al. (2020) (see text for more details). Temperatures are calculated using the parametrizations by Kim and O'Neil (1997) (T^a), Tremaine et al. (2011) (T^b), and Johnston et al. (2013) (T^c). Measurements with isotopic composition clearly off the MWL or poor reproducibility (marked with a *) are discarded from further paleo-climatic inferences from the temperature estimates (see text for more details).

Sample ID	No. of replic.	Age		water content	$\delta^{18}O_f$		$\delta^{2}H_f$		$\delta^{18}O_c$		T^a (Kim and O'Neil, (1997)		T^b (Tremaine et al., 2011)		T^c (Johnston et al., 2013)	
		[ka]	Δ	[µl/g]	[‰]	Δ	[‰]	Δ	[‰]	Δ	[°C]	Δ	[°C]	Δ	[°C]	Δ
1*	2	15.99	0.64	0.66	2.96	0.35	33.36	1.06	1.61	0.38						
5*	2	17.77	0.30	0.30	7.60	0.35	39.41	1.06	-0.75	0.38						
5b	2	18.00	0.31	0.40	-0.22	0.35	20.45	1.06	-0.85	0.44	16.6	1.6	22.7	1.9	21.3	1.7
7*	2	20.24	0.43	0.10	11.40	0.35	41.18	1.06	-0.02	0.38						
8	2	21.39	0.25	0.52	-1.72	0.35	18.53	1.06	-1.08	0.13	10.8	1.6	16.0	1.8	15.2	1.7
9b*	3	22.52	0.23	0.68	1.79	0.29	12.69	0.87	-1.16	0.15						
9*	2	22.63	0.21	0.38	4.03	0.35	17.35	1.06	-1.23	0.10						
10	3	23.54	0.17	1.86	-0.57	0.29	7.03	0.87	-1.22	0.15	16.6	1.3	22.8	1.6	21.4	1.4
12	2	24.25	0.22	0.71	1.34	0.35	12.41	1.06	0.48	0.21	17.7	1.7	24.0	1.9	22.5	1.7
13	3	24.63	0.26	2.01	-1.87	0.29	6.85	0.87	-1.50	0.16	12.0	1.3	17.4	1.5	16.5	1.4
14*	2	26.79	0.30	0.41	2.93	0.35	20.36	1.06	-0.62	0.28						
15	5	27.76	0.27	1.18	-0.48	0.22	13.35	0.67	-0.85	0.37	15.4	1.0	21.3	1.2	20.0	1.1
16	2	28.18	0.55	2.94	-0.06	0.35	10.50	1.06	-0.30	0.14	14.8	1.6	20.7	1.9	19.5	1.7
17*	2	29.32	0.22	0.39	6.44	0.35	27.49	1.06	0.01	0.48						
18	2	30.01	0.24	0.65	0.92	0.35	20.76	1.06	1.06	0.54	13.0	1.6	18.6	1.9	17.6	1.7
19	3	30.59	0.73	0.59	-0.36	0.29	16.63	0.87	-0.45	0.32	14.1	1.3	19.8	1.5	18.7	1.4
22*	2	32.24	0.41	0.17	8.25	0.35	40.63	1.06	-0.76	0.52						
23*	2	32.50	0.66	0.54	3.40	0.35	25.48	1.06	-0.93	0.16						
24	4	33.52	0.52	0.82	0.02	0.25	18.79	0.75	-0.05	0.35	19.1	1.2	25.7	1.4	24.0	1.2
24b*	2	33.56	0.33	0.24	9.56	0.35	31.11	1.06	-1.14	0.46						
25*	2	34.05	0.49	0.34	6.98	0.35	37.67	1.06	-1.49	0.07						
27*	3	35.32	0.35	0.58	0.64	0.29	16.80	0.87	-0.03	0.13						
28	3	35.63	0.40	1.65	0.21	0.29	13.56	0.87	-1.58	0.20	15.0	1.3	20.9	1.6	19.6	1.4
30*	2	41.73	0.21	0.30	10.36	0.35	44.94	1.06	-0.08	0.33						
31*	1	41.90	0.28	0.50	5.61	0.50	29.62	1.50	-0.26	0.28						
32*	1	42.99	0.43	0.55	0.81	0.50	20.03	1.50	-0.79	0.24						
32b*	2	43.01	0.47	1.02	8.47	0.35	27.21	1.06	-1.52	0.18						
33*	1	43.54	0.45	0.30	6.19	0.50	22.94	1.50	-1.43	0.17						
35	3	45.26	1.19	1.57	0.95	0.29	18.24	0.87	-0.40	0.32	17.1	1.3	23.4	1.6	21.9	1.4
36*	2	45.96	0.85	0.57	1.52	0.35	16.18	1.06	-0.90	0.28						

S.2 Supplementary figures

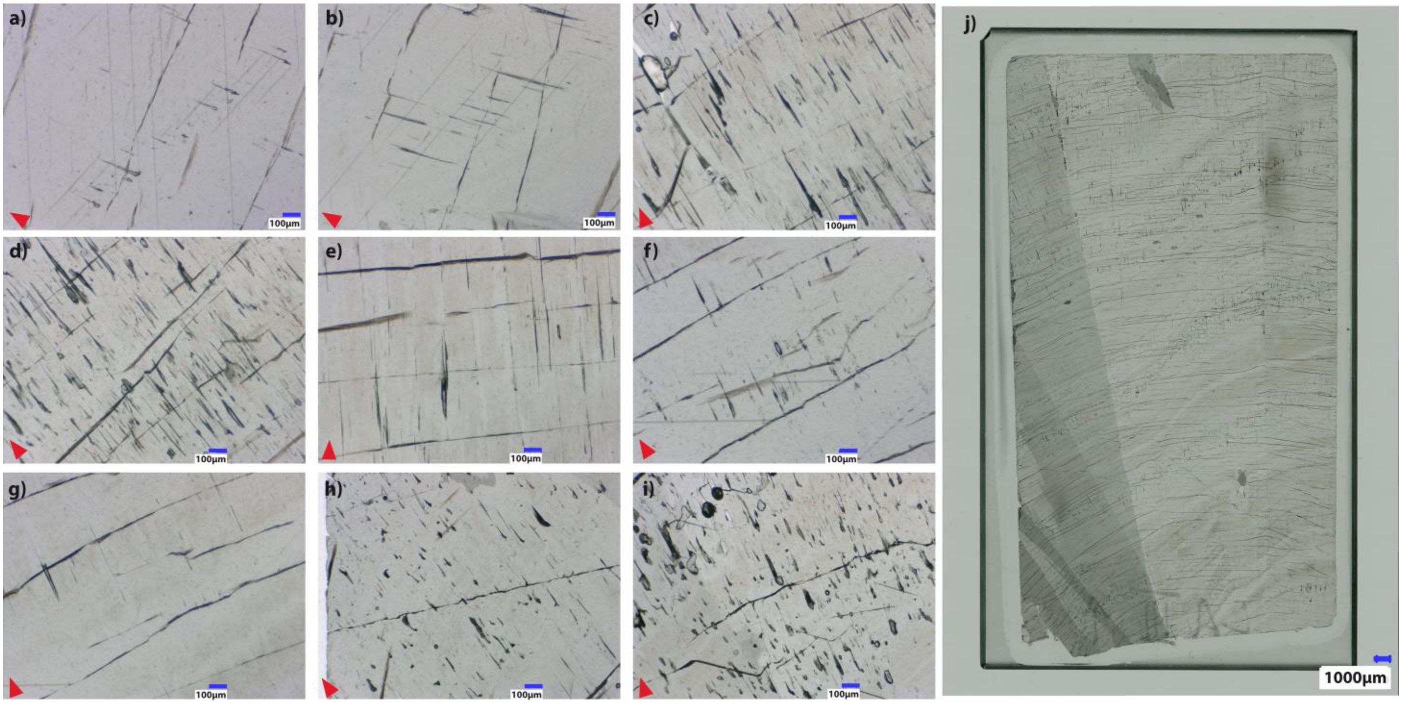

Figure S 1 Transmitted light photographs of polished thin sections of stalagmite PR-LA-1 (obtained with a Keyence VHX-6000 digital microscope) showing typical shapes and distribution of fluid inclusion. The photographs were taken from sections corresponding to depths of analysed fluid inclusion samples, where the red arrow shows the respective growth direction. (a) and (b) show examples of thin, elongated fluid inclusions from sections corresponding to samples 1, as well as 5 and 5b. (c) and (d) are examples of fluid inclusion rich parts corresponding to the depths of samples 19 and 20. (e), (f) and (g) are examples for sections with lower water content, and correspond to samples depths 21b, 22 and 23, respectively. (h) and (i) show examples of less elongated fluid inclusions corresponding to sample depths 27 and 27b, respectively. Lack of evidence of dissolution and/or recrystallization of calcite crystals suggests that fluid inclusions are pristine. The isotopic composition of fluid inclusion samples 1 (a), 21b (e), 27 (h) and 27b (i) show signs of evaporation, in contrast to samples 5b (b), 19 (c), 20 (d). In samples 22 (f) and 23 (g) the water content was too low for fluid inclusion analysis. j) Image of a whole thin section of PR-LA-1, illustrating the dominant fabric with large columnar calcite crystals. Petrography shows that no clear relationship can be found between shape and distribution of the fluid inclusions and the isotopic composition of the inclusion water.

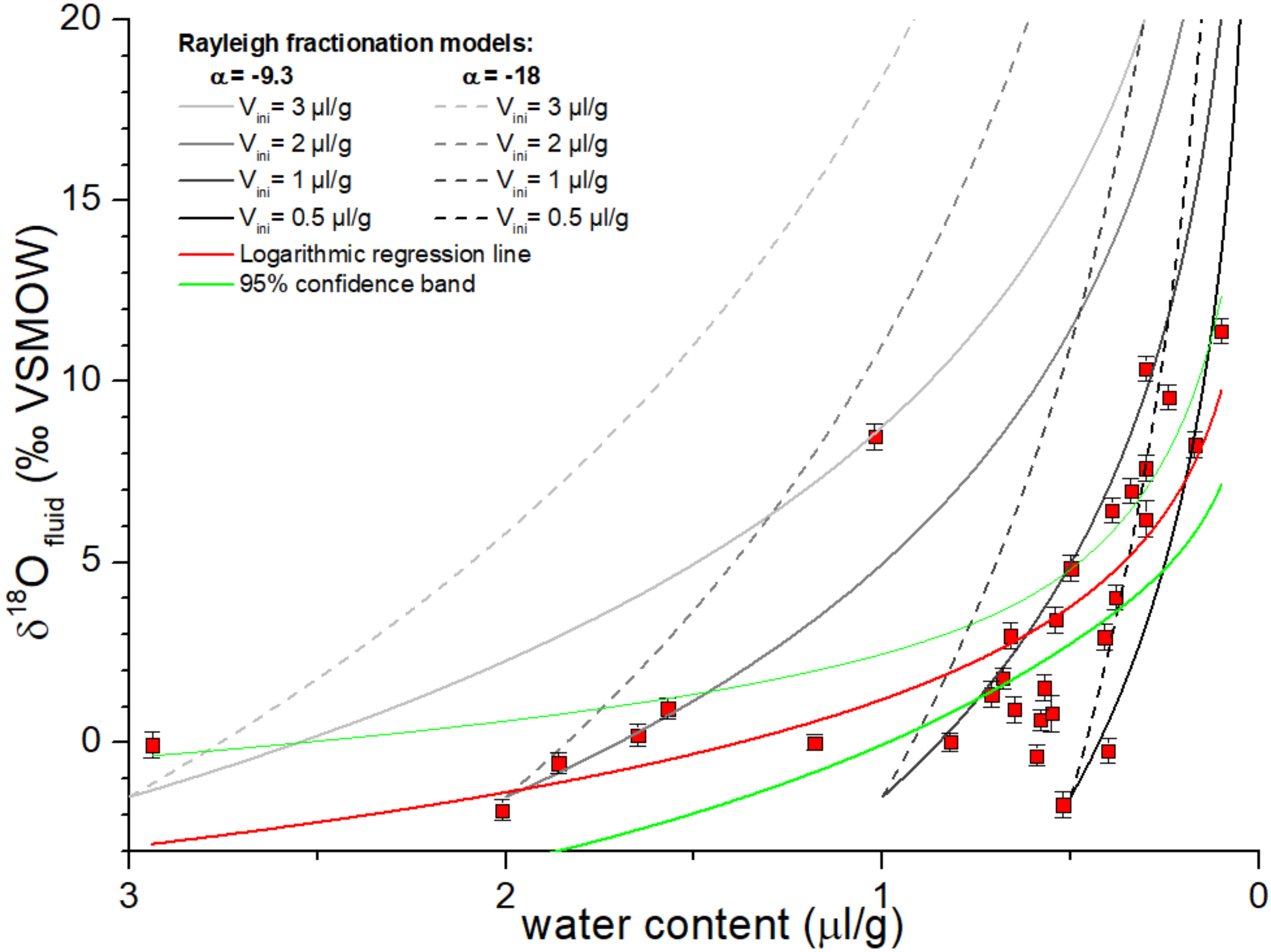

Figure S 2. Fluid inclusion stable isotope data (represented by $\delta^{18}O$ values) vs. measured water content. The data suggest an exponential enrichment of ^{18}O with decreasing water content (r = -0.72 for logarithmic fitting). Solid lines indicate Rayleigh fractionation with different initial water volumes V_{ini} and an equilibrium fractionation of 9.3‰ (Majoube, 1971). Since the kinetic fractionation factor under evaporative conditions is much higher, we also show the Rayleigh fractionation curves for a larger exemplary fractionation factor of 18‰. The Rayleigh curves demonstrate that the evolution may be explained by progressive evaporation of the water in the fluid inclusions before closure, and associated enrichment of the heavy stable water isotopes.

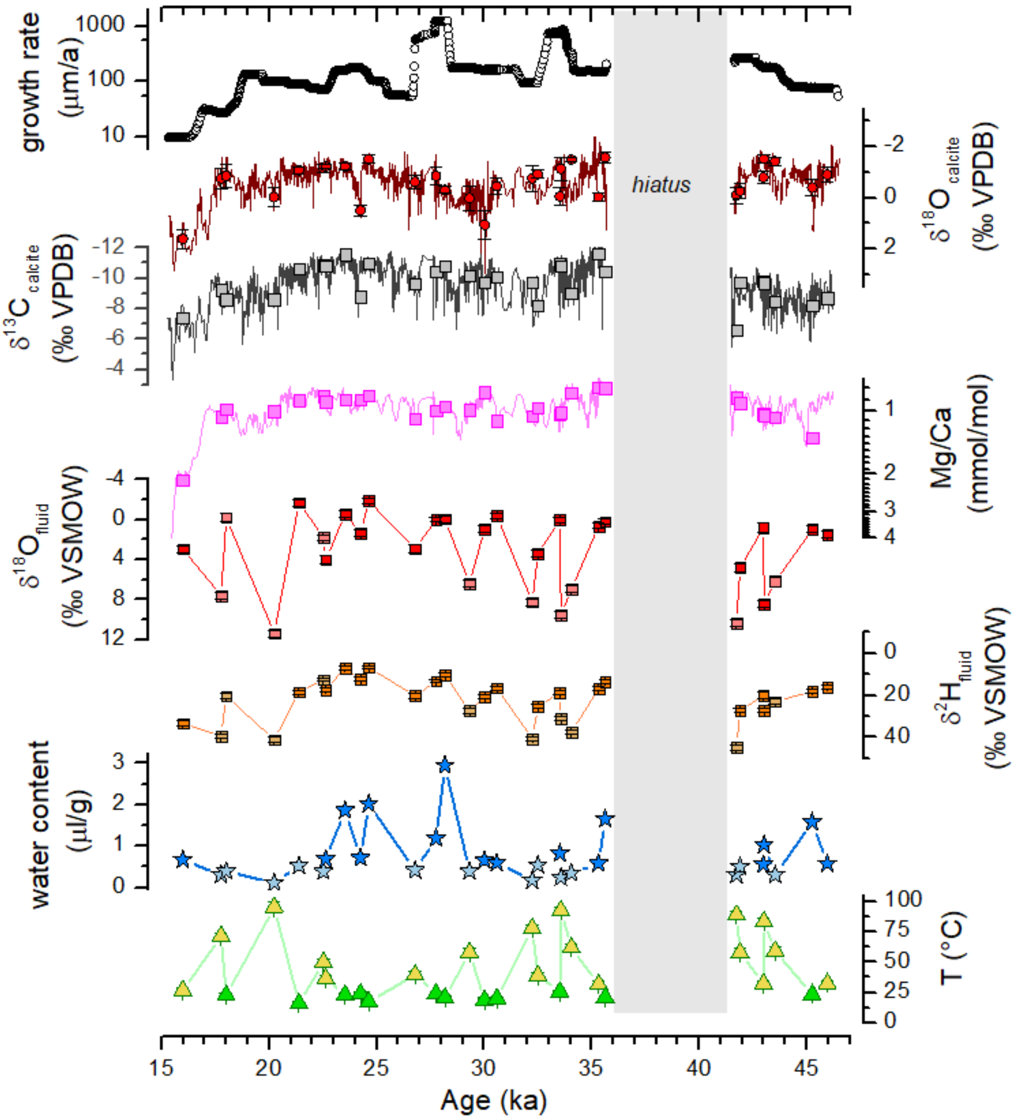

Figure S 3: Comparison of PR-LA-1 proxies including (from top to bottom) the growth rate (black) as well as calcite δ^{18}O (dark red), δ^{13}C (dark grey), and Mg/Ca (magenta) values (Warken et al., 2020). Lines indicate the unsmoothed data, symbols the averaged values for the depth range covered by the fluid inclusion samples, respectively. Fluid inclusion data include δ$^{18}O_f$ (red), δ$^{2}H_f$ (orange), and the measured water content (blue). Symbol colors indicate the samples with high (dark colored symbols) and low (light colored stars) water content with a threshold value of 0.55 µl/g, respectively. The bottom-most panel shows the temperatures from the fractionation between fluid inclusion and speleothem calcite δ^{18}O values. Yellow colors indicate temperatures which are regarded as not reliable, while green symbols indicate reasonable paleo-temperatures, as discussed in the main manuscript.