

1 **Supplementary data:**

2 **Calculation of Δ_{47} values in the absolute reference frame**

3 Δ_{47} values in the main text are reported using the original clumped isotope reference
4 frame, as was used in the Δ_{47} -T calibration of Ghosh et al. (2006) (noted as ‘lab frame’). The
5 data in Table S1 is also given using a new absolute reference frame (defined by Dennis et al.,
6 2011). The absolute reference frame is based on the measurement of CO₂ equilibrated with
7 H₂O at different temperatures having defined absolute Δ_{47} values that are based on *ab-initio*
8 calculations (Wang et al., 2004).

9 The conversion of Δ_{47} values from the laboratory frame to the absolute frame uses the
10 long-term average of laboratory standards (Carrara Marble, CO₂ gas equilibrated with water at
11 25 °C, CO₂-gas standard). The heated gas value at 1000 °C is considered as an additional
12 calibration point in the calculation.

13 **Evaluation of the speleothem fluid inclusion noble gas data**

14 Noble gases and water were liberated from the stalagmite samples in a stepwise
15 procedure. This stepwise extraction leads sometimes to differences between subsequent steps
16 due to preferential opening of inclusions of a certain size (Marx and Aeschbach-Hertig,
17 2012). In the first step mostly large air-filled inclusions at grain boundaries are opened,
18 whereas in later steps the gases increasingly originate from smaller, intra-crystalline water-
19 filled inclusions (Scheidegger et al., 2011). To avoid aliasing we take the combined noble gas
20 concentration of all steps as most reliable. In cases where the combined signal could not be
21 used (e.g. due to a too high air/water volume ratio, Kluge et al., 2008) we evaluated the single
22 steps by the inverse method of Aeschbach-Hertig et al. (1999) and selected the extraction step
23 with the best fit, namely the step with the lowest χ^2 . We use χ^2 , the sum of the error-weighted
24 squared deviations of the measured noble gas concentration from the modeled concentrations,
25 to judge the quality of the fit. The expectation value for χ^2 is 2 (four measured concentrations

1 and two free parameters) and with a probability of 0.99 to be smaller than 9.2. χ^2 values above
2 9.2 indicate a bad fit and are therefore generally rejected. Noble gas concentrations, χ^2 , and
3 the fitted temperature of the relevant extraction steps are summarized in Table S2.

4 **Additional references**

5 Marx, T. and Aeschbach-Hertig, W.: Challenges on the way to noble gas temperatures on
6 speleothems, Geophys. Res. Abstracts, 14, EGU2012-9621, 2012.

1 **Table S1:**

2 Δ_{47} values in original reference frame (lab frame) and newly defined absolute reference frame
 3 (Dennis et al., 2011).

Sample	Δ_{47} lab frame (‰)	$\Delta_{47, \text{abs}}$ (‰)
Modern set		
DC-1	0.648±0.005	0.708±0.006
DC-2	0.657±0.004	0.718±0.005
HC-1	0.674±0.004	0.736±0.004
HC-2	0.687±0.004	0.749±0.005
HC-3	0.671±0.002	0.732±0.002
HC-4	0.689±0.001	0.751±0.002
B7-B01	0.668±0.006	0.729±0.007
U I-4	0.668±0.020	0.729±0.021
U I-16	0.665±0.008	0.726±0.009
U IV-15	0.638±0.020	0.697±0.021
U VII-5	0.670±0.020	0.731±0.021
U VII-8	0.653±0.020	0.713±0.021
U VII-14	0.675±0.020	0.737±0.021
U VII-15	0.658±0.003	0.718±0.003
Stalagmite BU1		
1	0.659±0.007	0.720±0.007
2	0.673±0.002	0.734±0.002
3	0.670±0.009	0.731±0.010
4	0.685±0.002	0.748±0.002
5	0.676±0.005	0.738±0.005
6	0.679±0.003	0.740±0.003
7	0.678±0.008	0.740±0.009
8	0.681±0.007	0.743±0.007
9	0.693±0.002	0.755±0.002
10	0.671±0.007	0.732±0.008
Stalagmite BU4		
1	0.668±0.007	0.729±0.007
2	0.677±0.003	0.739±0.003
3	0.671±0.003	0.732±0.003
4	0.669±0.007	0.731±0.007
5	0.677±0.006	0.739±0.006
6	0.667±0.004	0.728±0.004
7	0.676±0.004	0.738±0.004
8	0.692±0.005	0.754±0.005
9	0.705±0.005	0.768±0.005

Stalagmite BU2

1	0.674±0.007	0.735±0.007
2	0.669±0.005	0.730±0.005
3	0.702±0.007	0.765±0.007
4	0.696±0.007	0.759±0.008

Stalagmite BU-UWE

1	0.667±0.005	0.728±0.005
2	0.663±0.005	0.724±0.006
3	0.663±0.004	0.723±0.004
4	0.692±0.005	0.754±0.005
5	0.662±0.008	0.722±0.008
6	0.668±0.003	0.729±0.003
7	0.676±0.011	0.738±0.011

1 **Table S2:** Noble gas concentrations (in ccSTP per g water), χ^2 , extraction steps used for
 2 inverse modeling, and NGTs of stalagmite BU1. Data of BU-UWE (Kluge et al., 2008) are
 3 given for completeness. The extraction typically consists of 2-3 crushing steps and a final
 4 heating step. The first extraction step was normally discarded due to a high air contribution.

Sample	Ne (10^{-7} cc/g)	Ar (10^{-4} cc/g)	Kr (10^{-7} cc/g)	Xe (10^{-8} cc/g)	χ^2 (-)	Used extraction steps	NGT (°C)
BU 1-A	17.1±0.3	11.3±0.2	1.87±0.04	2.17±0.04	4.9	All ^a	7.1±0.8
BU1-B	8.3±0.3	7.6±0.2	1.40±0.05	1.68±0.07	3.0	thermal extraction step	7.1±1.1
BU1-C	23.8±0.5	14.9±0.3	2.28±0.05	2.51±0.08	1.7	all except first	7.3±1.4
BU1-D I	76.6±2.5	40.5±1.4	5.5±0.2	4.9±0.2	0.9	all except first	9.8±5.6
BU1-D II	20.7±0.5	12.9±0.2	2.04±0.04	2.21±0.06	2.8	all except first	9.5±1.3
BU1-E	36.7±0.7	21.9±0.4	3.16±0.07	3.04±0.08	0.3	all	7.9±1.6
BU1-F	4.3±0.3	5.2±0.2	1.08±0.04	1.43±0.06	0.7	all except first	9.0±1.1
BU1-G I	5.6±0.6	5.6±0.5	1.11±0.09	1.5±0.1	0.1	thermal extraction step	10.0±2.3
BU1-G II	-	7.57±0.09	1.44±0.03	1.70±0.04	4.6	all except first	7.5±0.9
BU-UWE							
Early Holocene					1.1-9.3	see Kluge et al. (2008)	1.7-3.6

5 ^a only one extraction step (crushing)