Summer school Environmental History and Historical Ecology of the Dinaric Karst, Slovenia, Slovenia, 25–30 September 2023

Paleoclimate records from speleothems: an example from the Dinaric karst in Slovenia

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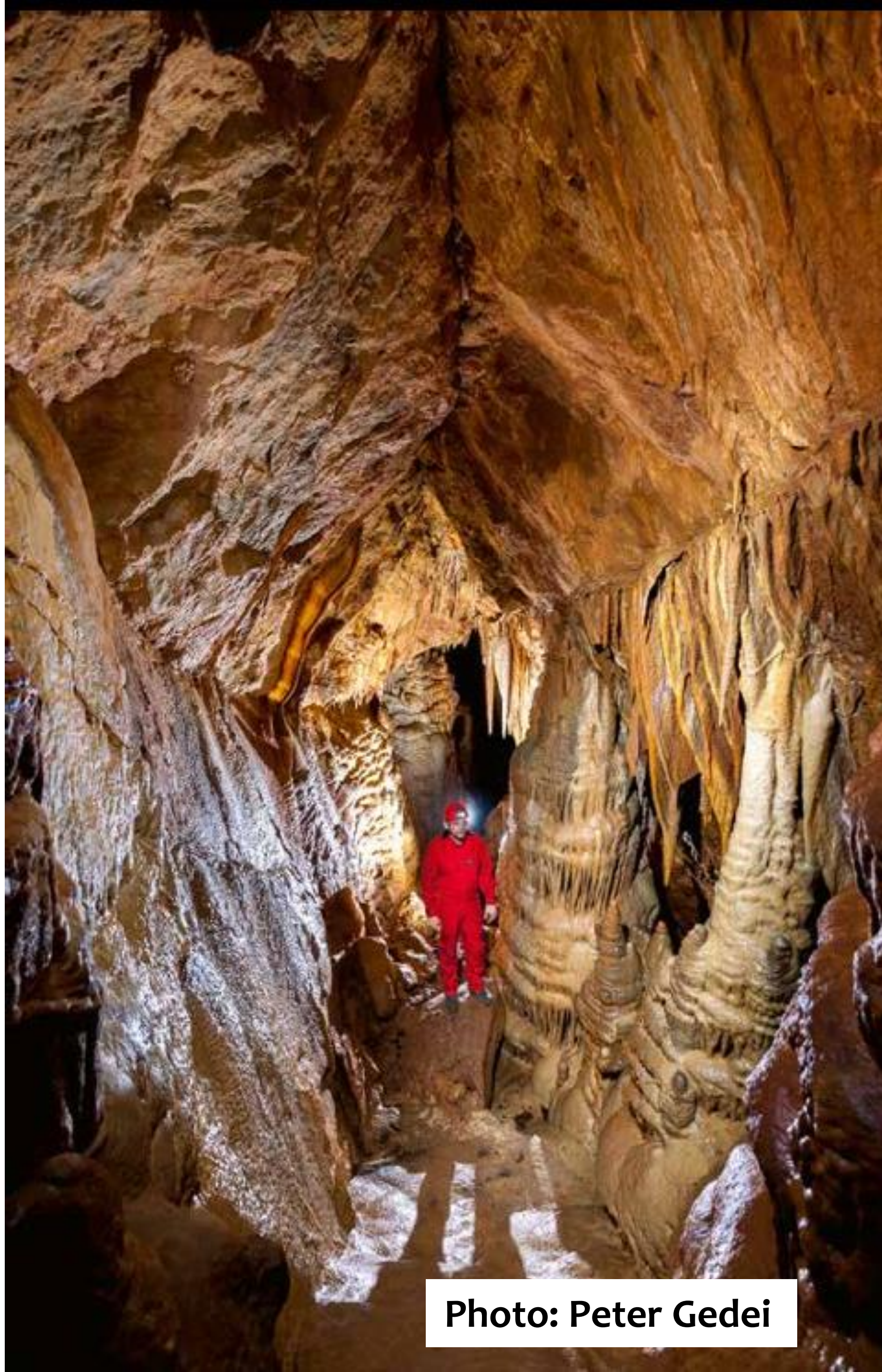
Why speleothems?

→ chemical precipitates – reflect the ambiental physico-chemical conditions

→ stable environment compared to the Earths‘s surface

→ grow slowly (growth rates of the order of magnitude ~ 1 μm to ~100 μm)



What makes a speleothem: isotopic and chemical composition of dripstone depends upon…

precipitation ⟶ dripwater ⟶ stalagmite

Regional-specific	Site-specific	Site-specific
Climate Continental effect Altitude effect Latitude effect Amount effect Moisture sources (atmospheric mass circulation)	Infiltration Geometry of aquifer (MTT, homogenisation) Water-rock interaction Cave climate (temperature, ventilation)	Cave climate Drip (flow) rate Biofilm

Karst aquifer

Conduits: joints enlarged by dissolution – fast conduit flow

Secondary - fractured porosity: joints, fault planes medium/high permeability

Primary porosity: low permeability

Stalagmite – how to interpret C and O isotopic profiles?

δ^{18}O: temperature record, based on the T-dependent isotope fractionation between O in water and carbonate

temperature↑ –δ^{18}O value↓

$T(°C)=16.5-4.3(\delta c-\delta w)+0.14(\delta c-\delta w)^2$ (Friedman, O'Neil 1977)

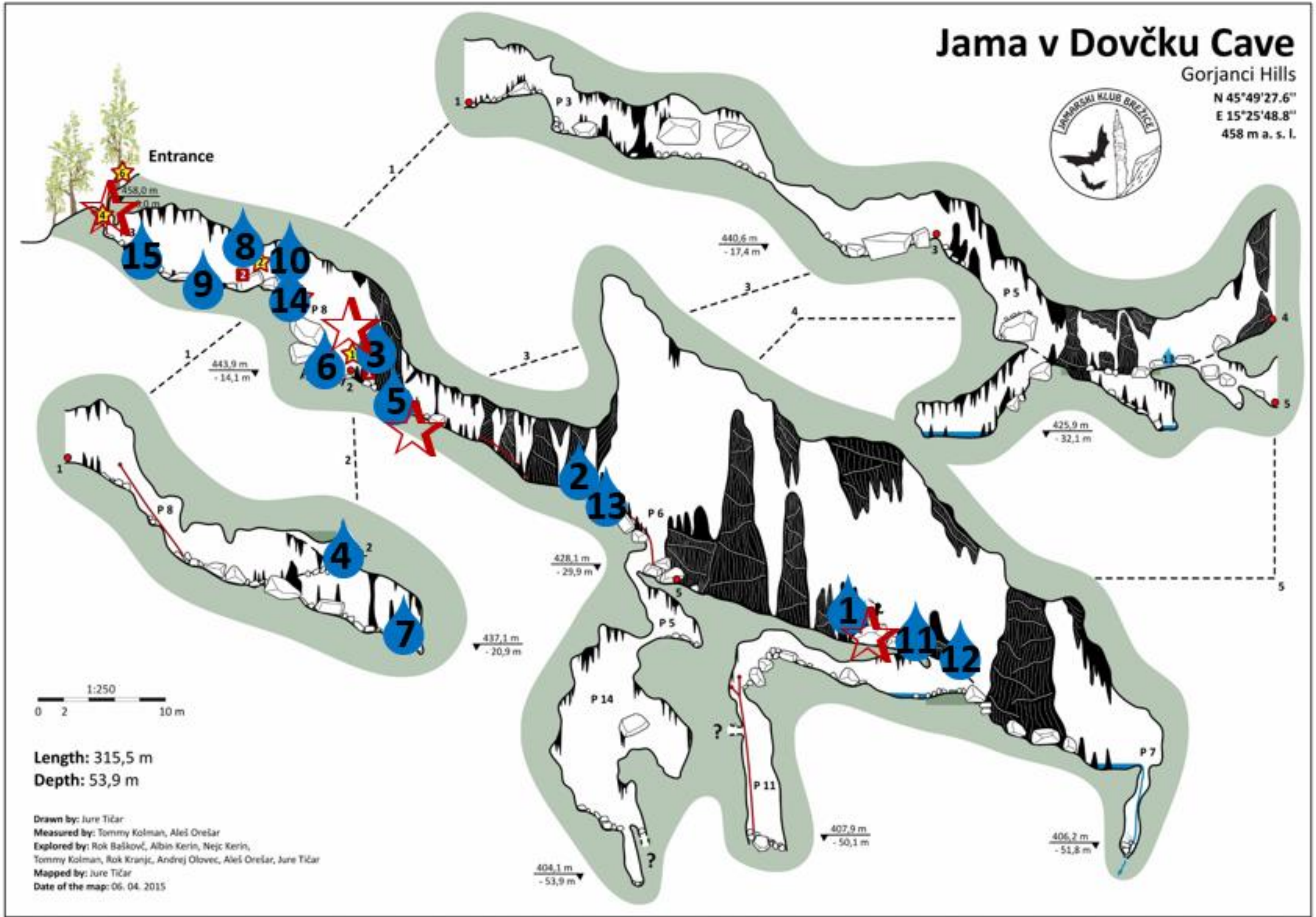
$1000 \ln \alpha = E\frac{(10^3)}{T}+F$ *E: 18.03; F: -32.42 Kim & O'Neil 1997*

$1000 \ln \alpha = D\frac{(10^6)}{T^2}+E\frac{(10^3)}{T}+F$ *D: 4.010; E: -4.66; F: 1.71 Zheng, 1999*

D: 2.789; E: 0.00; F: -2.89 Horita 2014

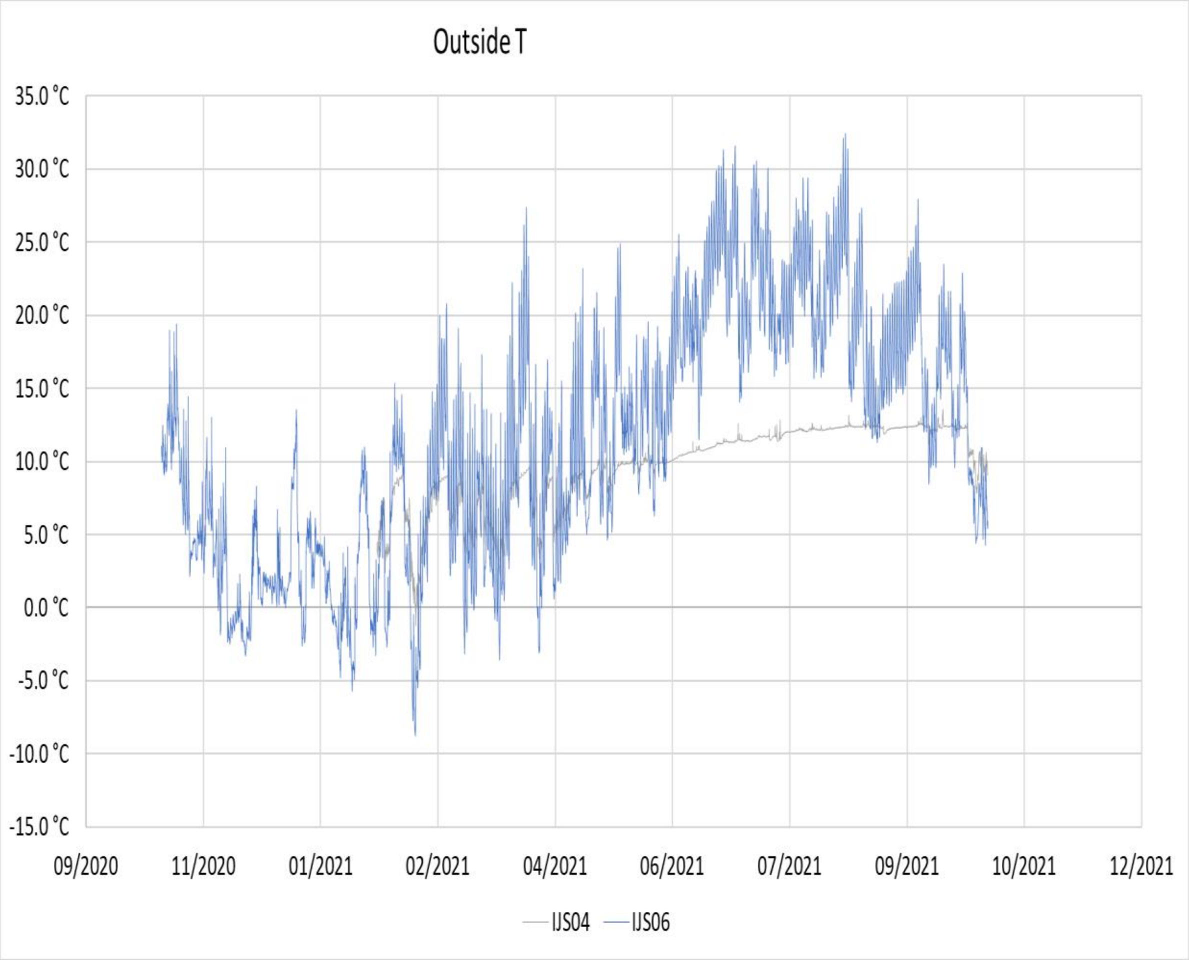
δ^{13}C: multiple influences – origin of C (organic/carbonate), vegetation, PCP, ventilation…. can be, but must not necessarily be linked to climate

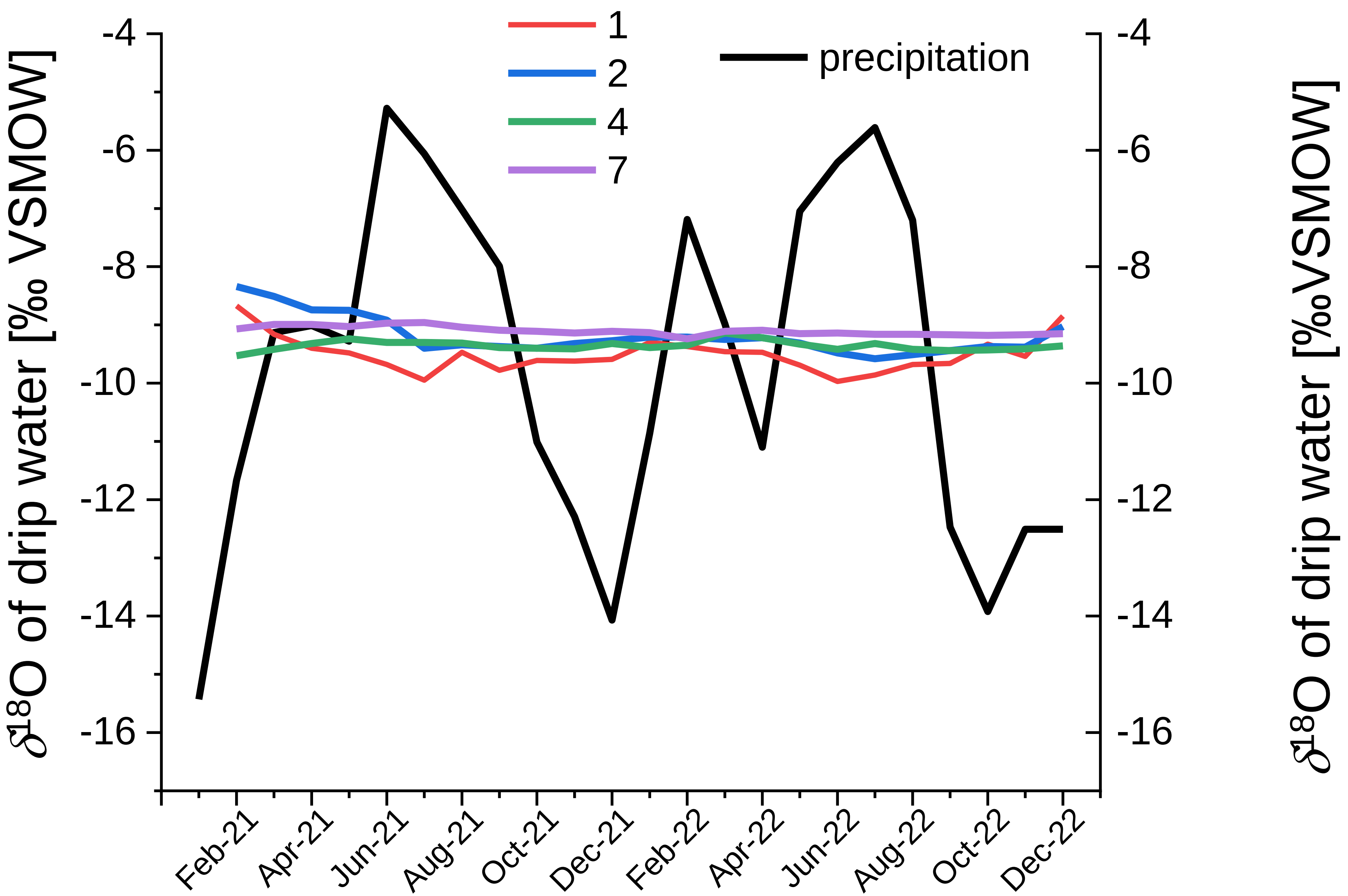
Example: Jama v Dovčku


Jama v Dovčku Cave
Gorjanci Hills
N 45°49'27.6''
E 15°25'48.8''
458 m a. s. l.
JAMARSKI KLUB BREŽICE
Entrance
458,0 m
443,9 m
- 14,1 m
440,6 m
- 17,4 m
437,1 m
- 20,9 m
428,1 m
- 29,9 m
425,9 m
- 32,1 m
407,9 m
- 50,1 m
406,2 m
- 51,8 m
404,1 m
- 53,9 m
P 3
P 5
P 6
P 7
P 8
P 11
P 14
1:250
0 2 10 m
Length: 315,5 m
Depth: 53,9 m
Drawn by: Jure Tičar
Measured by: Tommy Kolman, Aleš Orešar
Explored by: Rok Baškovč, Albin Kerin, Nejc Kerin,
Tommy Kolman, Rok Kranjc, Andrej Olovec, Aleš Orešar, Jure Tičar
Mapped by: Jure Tičar
Date of the map: 06. 04. 2015

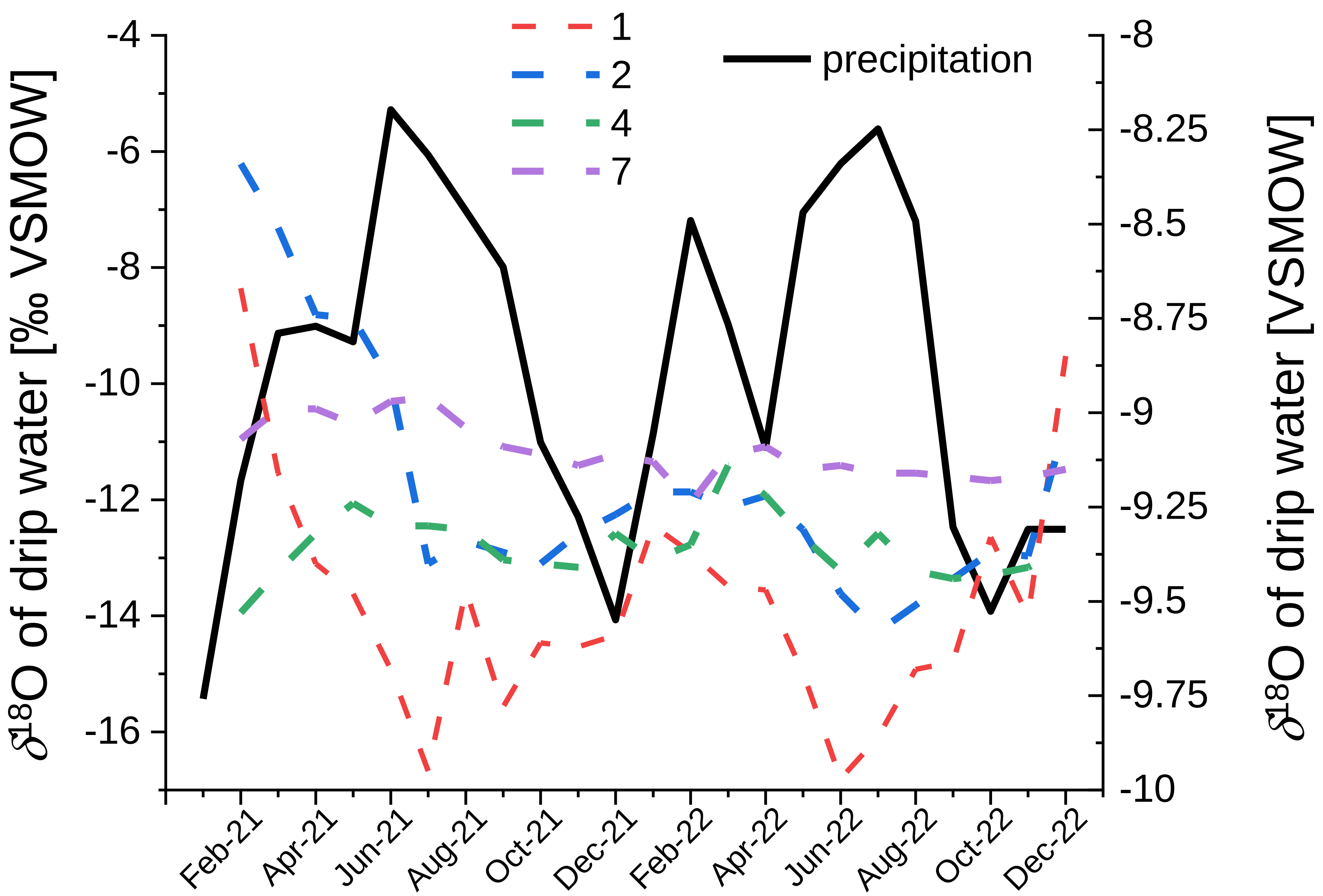
Entrance to the cave: avg. T = 8.4°C

16 m: 9.90 ± 0.13 °C
37 m: 9.73 ± 0.01°C





1
2
4
7
precipitation
-4
-6
-8
-10
-12
-14
-16
δ18O of drip water [‰ VSMOW]
δ18O of drip water [‰VSMOW]
Feb-21
Apr-21
Jun-21
Aug-21
Oct-21
Dec-21
Feb-22
Apr-22
Jun-22
Aug-22
Oct-22
Dec-22



1
2
4
7
precipitation
δ18O of drip water [‰ VSMOW]
δ18O of drip water [VSMOW]
-4
-6
-8
-10
-12
-14
-16
-8
-8.25
-8.5
-8.75
-9
-9.25
-9.5
-9.75
-10
Feb-21
Apr-21
Jun-21
Aug-21
Oct-21
Dec-21
Feb-22
Apr-22
Jun-22
Aug-22
Oct-22
Dec-22

Mean travel time of water → temporal resolution: year to decade

Sine-wave model*:

$$\delta^{18}O = \delta^{18}O_{mean} + A \cdot [\cos(c \cdot t - \theta)]$$

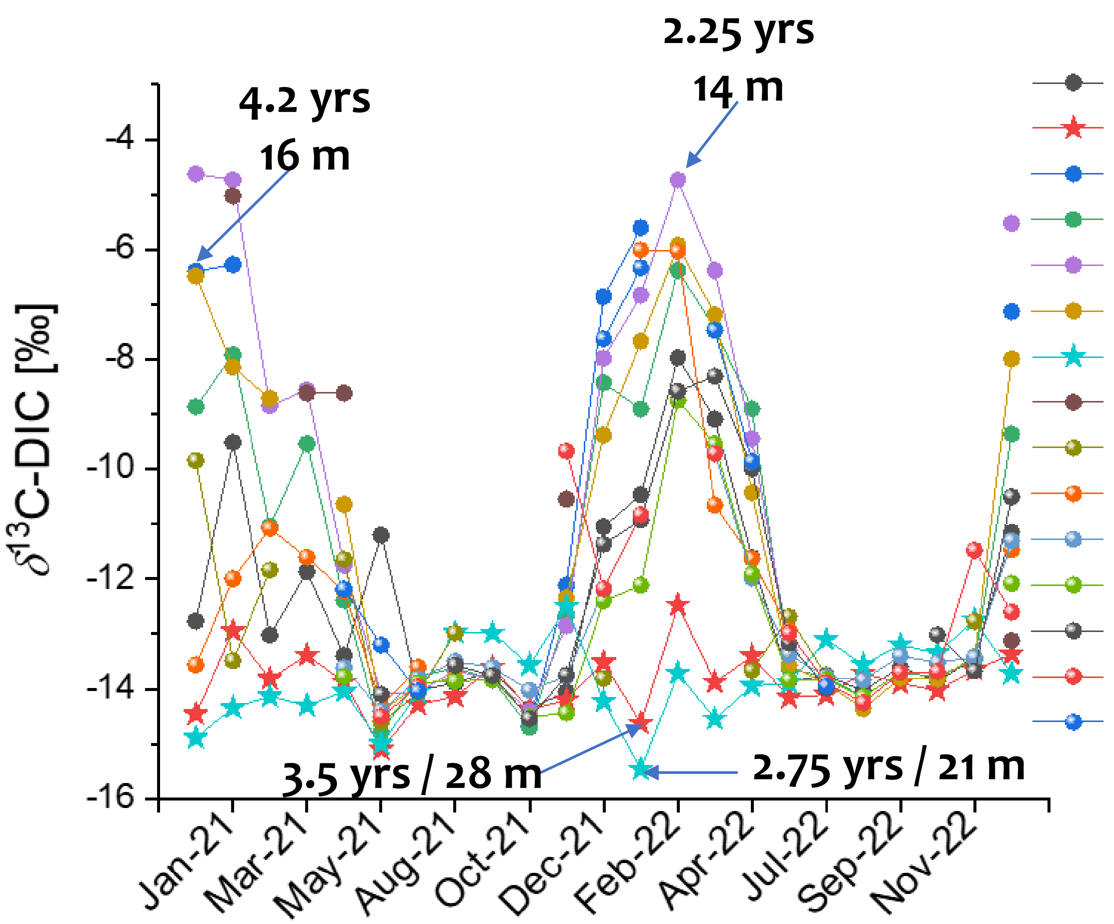
$$MTT = c^{-1} \cdot [(A_d/A_p) - 1]^{1/2}$$

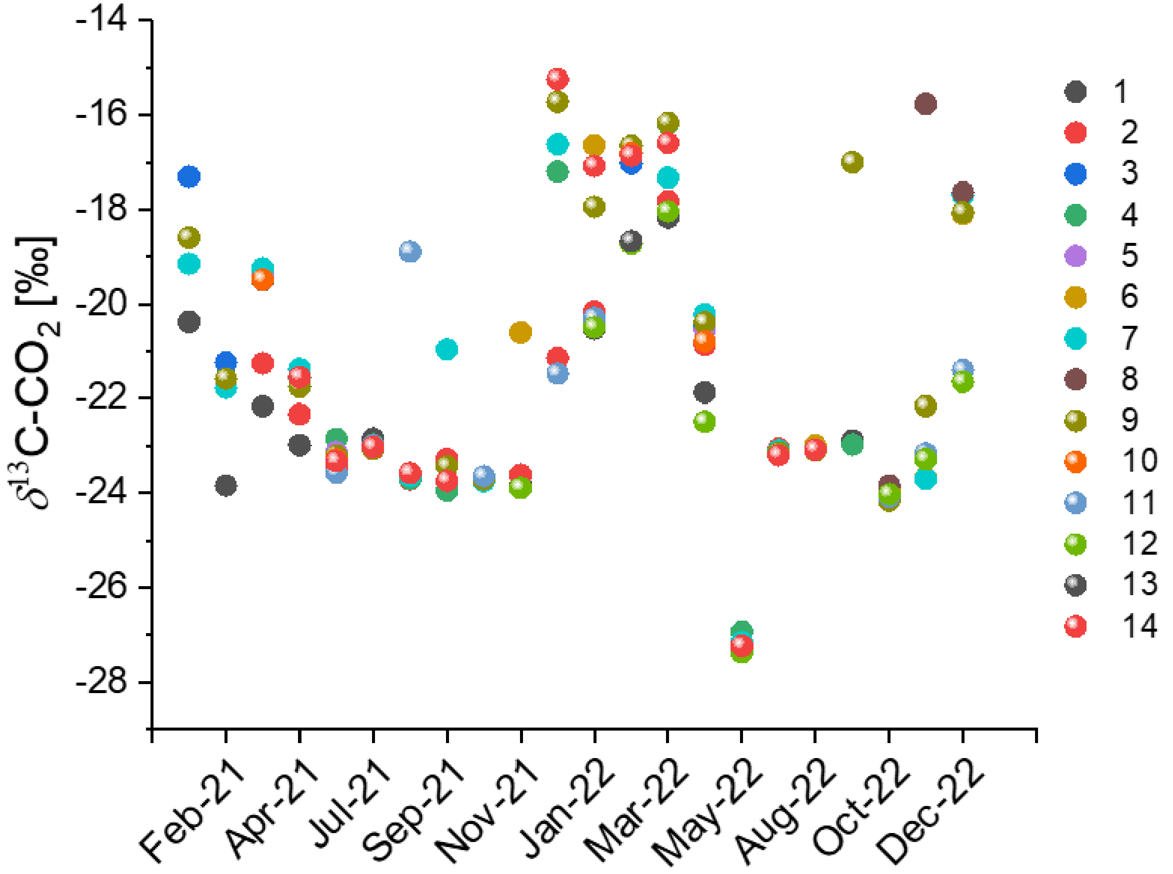
A = amplitude of drip water and precipitation
c = radial frequency of annual fluctuation
t = time (days)
θ = phase lag

Site	Roof [m]	MTT $\delta^{18}O$ [month]
15	0.9	17
9	1.6	22
14	3.1	28
10	3.5	37
8	4.8	30
5	13.8	27
6	16.2	50
3	16.6	22
4	16.9	24
7	21.3	33
2	28.0	42
13	28.9	37
11	37.0	38
1	37.3	20
12	49.1	40

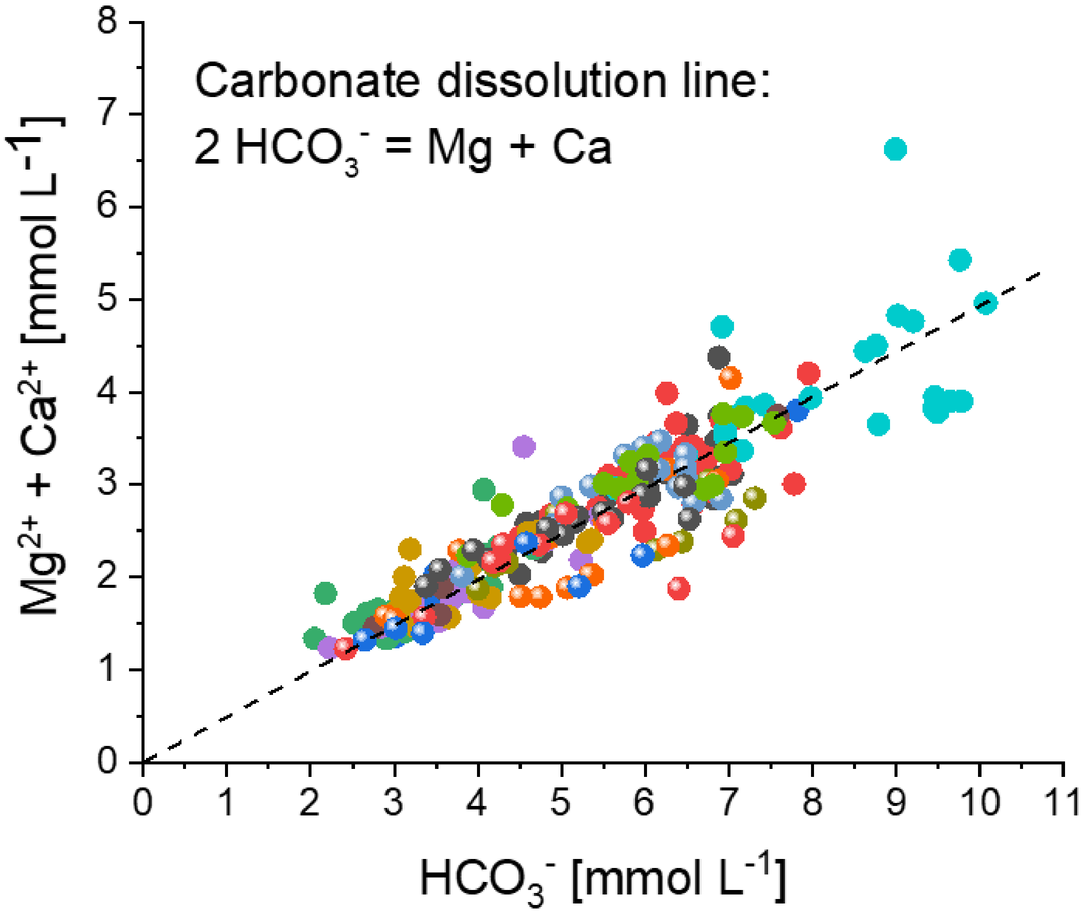
*Rodgers et al., Hydrol. Earth. Sys. Sci. 2005, 9, 139-155

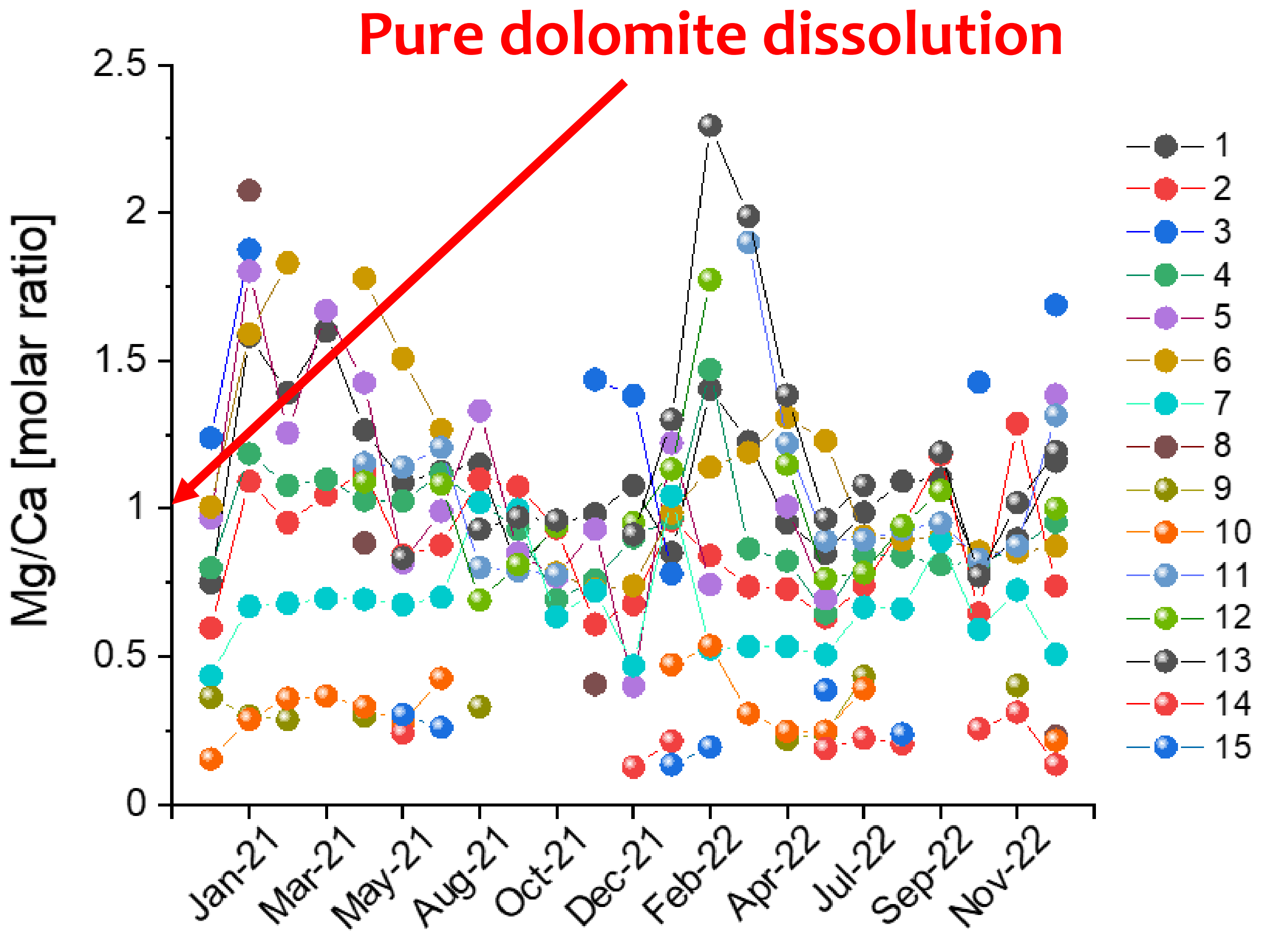
Dissolved inorganic C: seasonality in spite of long MTT





Water-rock interaction: Mg/Ca ratoios



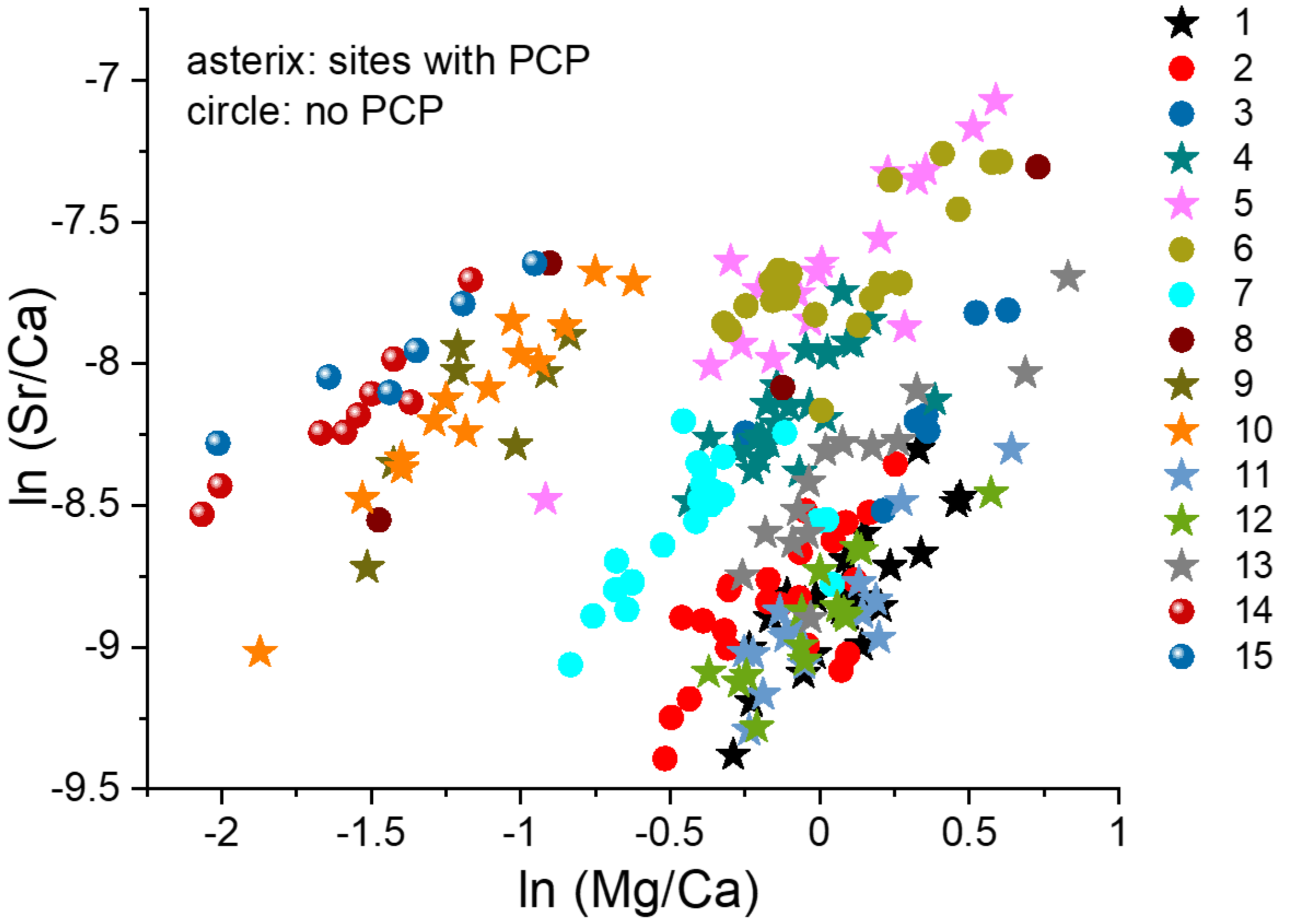


Prior calcite precipitation: Sinclair test#*

- correlated ln (Mg/Ca) and ln (Sr/Ca)
- slope between 0.71 and 1.45

PCP confirmed at 8 out of 15 sites (1, 4, 5, 9-13).

Speleothems for analysis: 3, 8



#Sinclair et al., Chem. Geol. 2012, 294-295, 1-17.
*Wassenburg et al., Geochim. Cosmochim. Acta 2020, 269, 581-596.

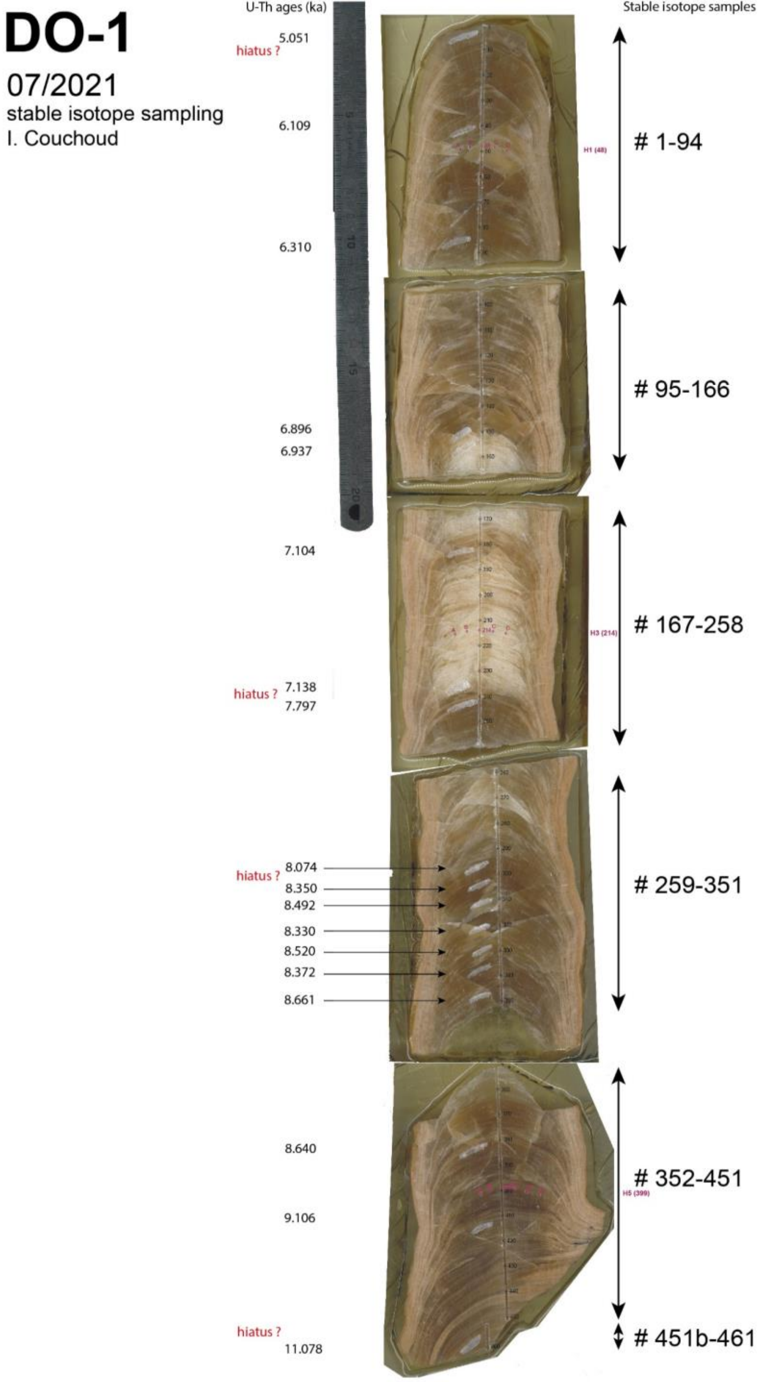
What did we learn from the dirp-water monitoring?

→ MTT of DW feeding analysed stalagmites most probably > 2 years, which doesn‘t exclude seasonality

→ considering the MTT, the biannual to decadal time resolution of the O isotope profile should be expected

→ PCP unlikely to affect the Mg/Ca and Sr/Ca ratios of cabonate, i.e., the geochemical thermometer could potenitally be used

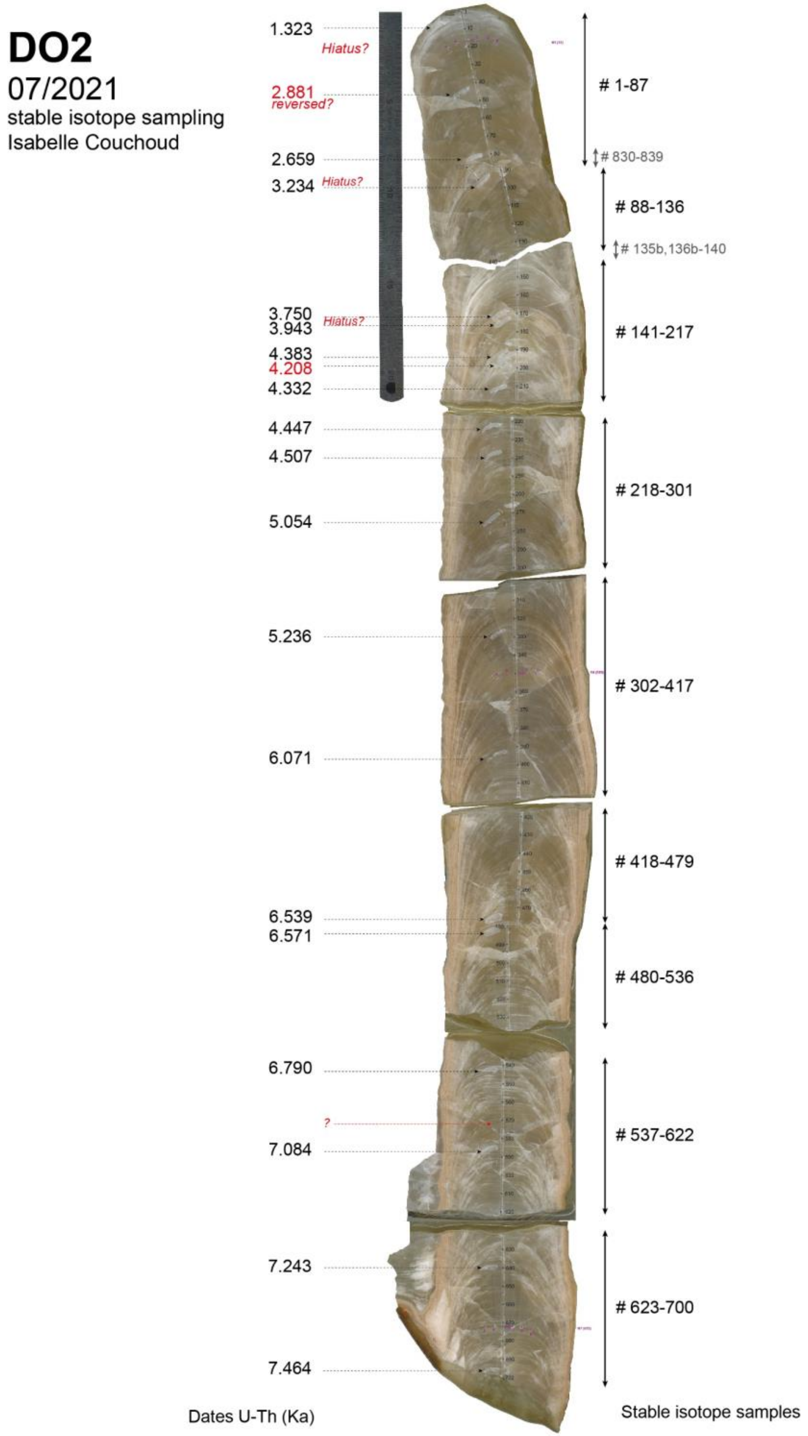
→ C isotopes: DIC is mostly in equilibrium with the cave atmosphere, at the locus of the harvested stalagmites the seasonality probably influences the $\delta^{13}C$ of carbonate



Two stalagmites: DO-1 and DO-2

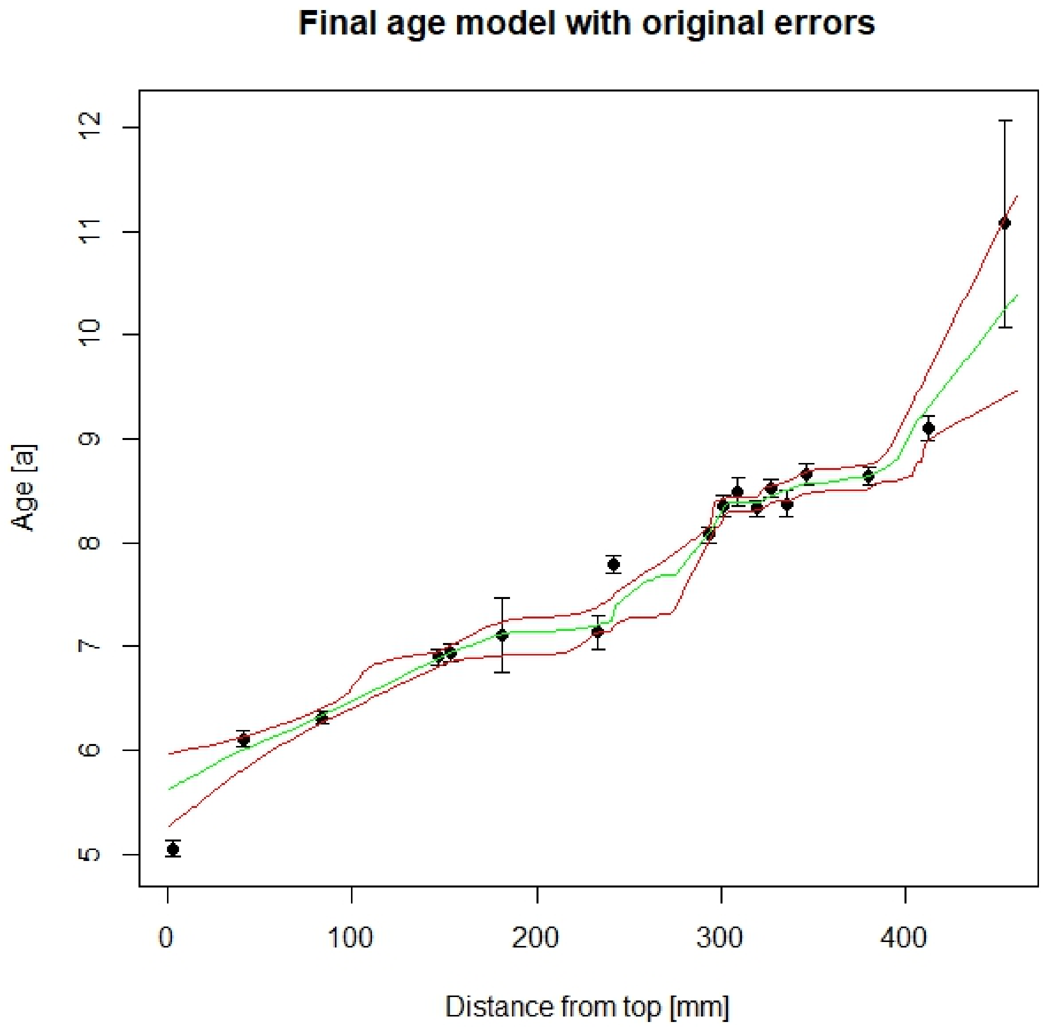
DO-1:
- 461 mm long
- spans from 11 ka to 5 ka

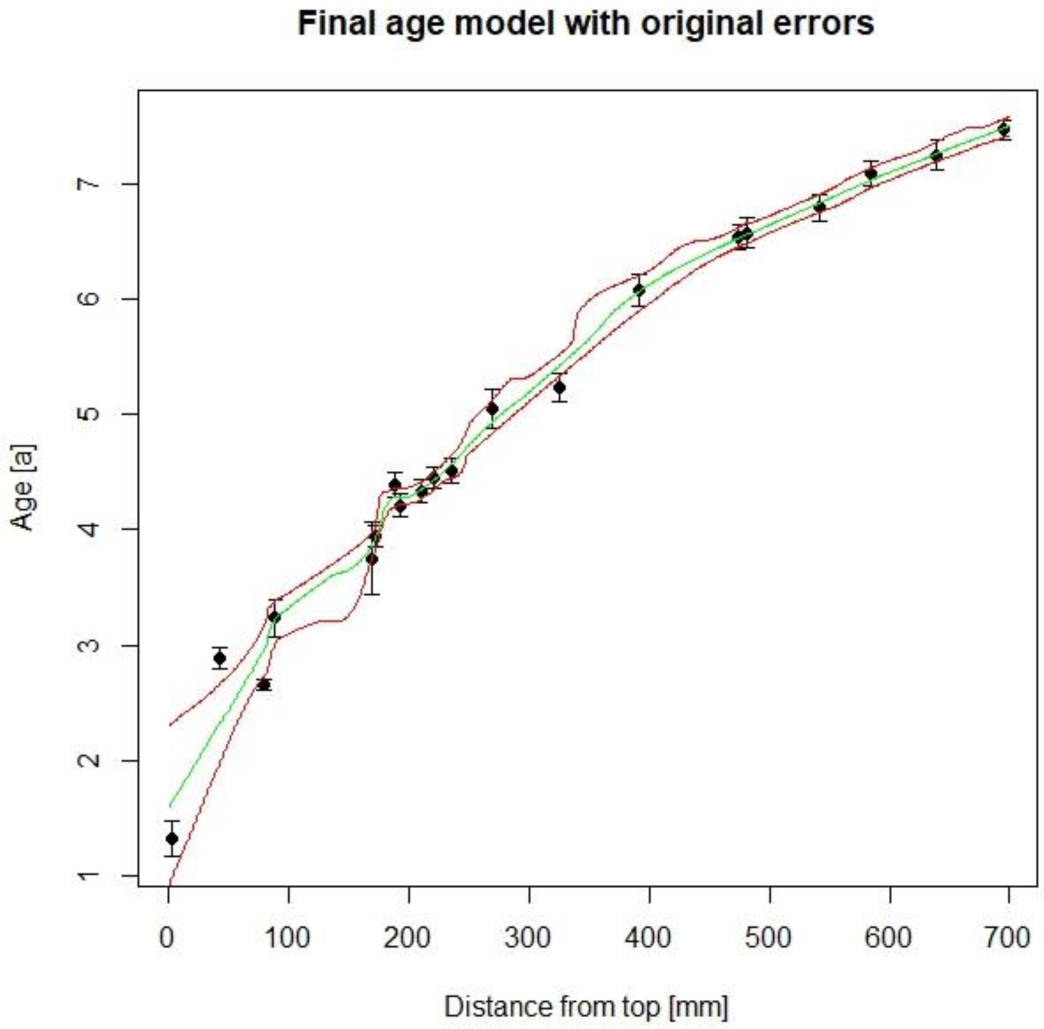
DO-2
- 700 mm long
- spans from 7.5 ka to 1.3 ka

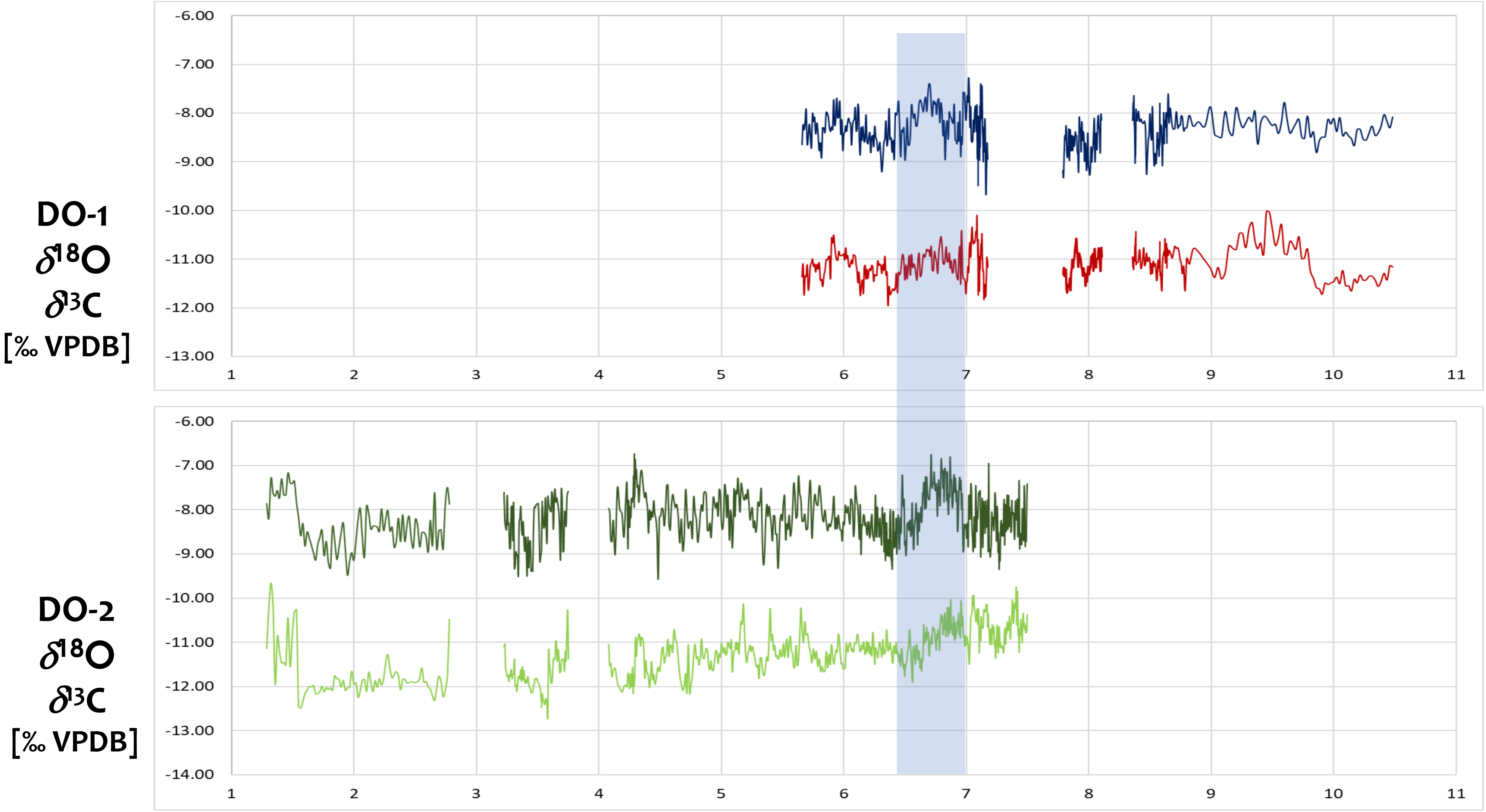


AGE DEPTH MODELLING BASED ON „StalAge“ BY SCHOLZ & HOFFMANN

- cca 20 U-Th ages for each stalagmite
- visible hiatuses






DO-1
δ18O
δ13C
[‰ VPDB]
-6.00
-7.00
-8.00
-9.00
-10.00
-11.00
-12.00
-13.00
1
2
3
4
5
6
7
8
9
10
11
DO-2
δ18O
δ13C
[‰ VPDB]
-6.00
-7.00
-8.00
-9.00
-10.00
-11.00
-12.00
-13.00
-14.00
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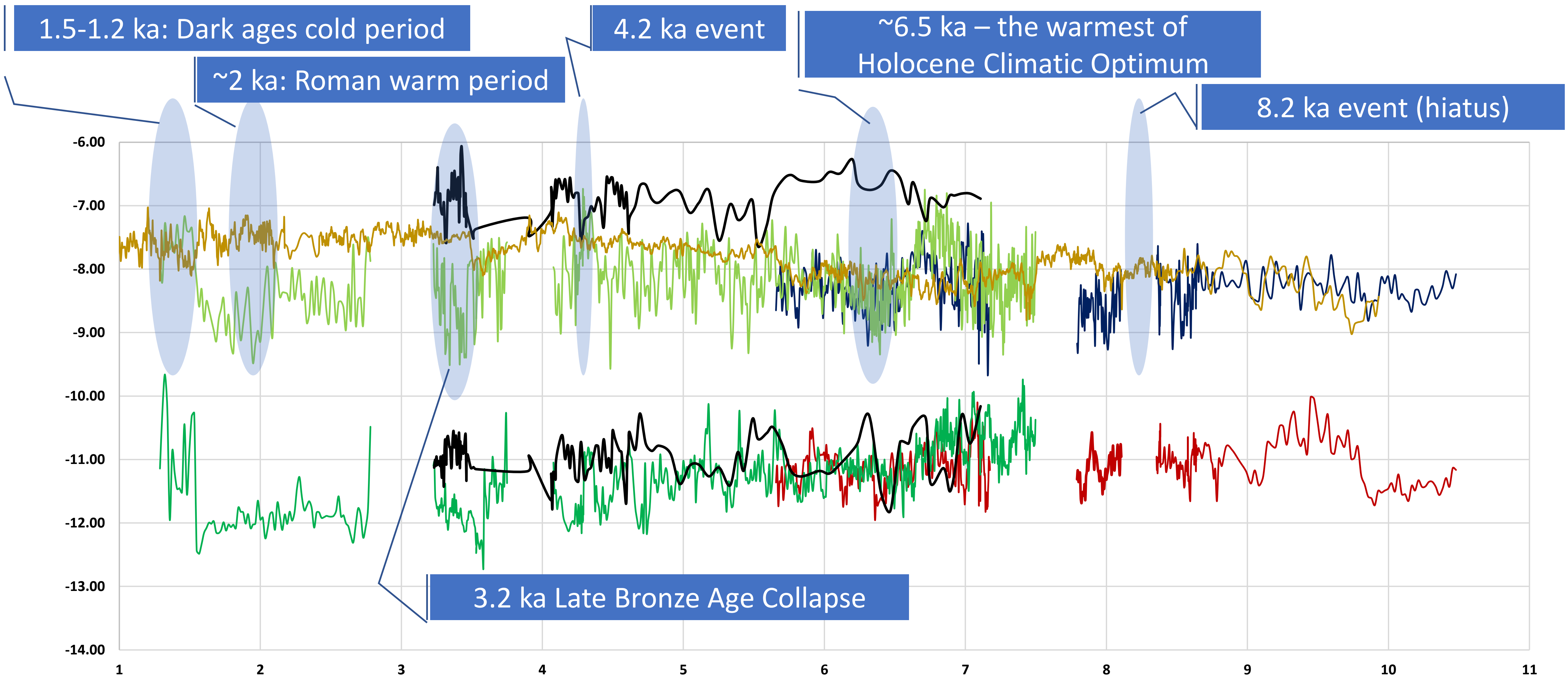
11

DO-1 and DO-2 + Postojna Cave & Spannagel Cave (Fohlmeister et al. 2013)

- Notable disturbance around 3.5 ka – 4 ka
- $\delta^{18}O$ from Postojna Cave tends to mirror $\delta^{18}O$ from Dovček Cave



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