Understanding the deglacial relationship between carbon isotopes and temperature in stalagmites from Western Europe

Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

UNIVERSITY OF OXFORD

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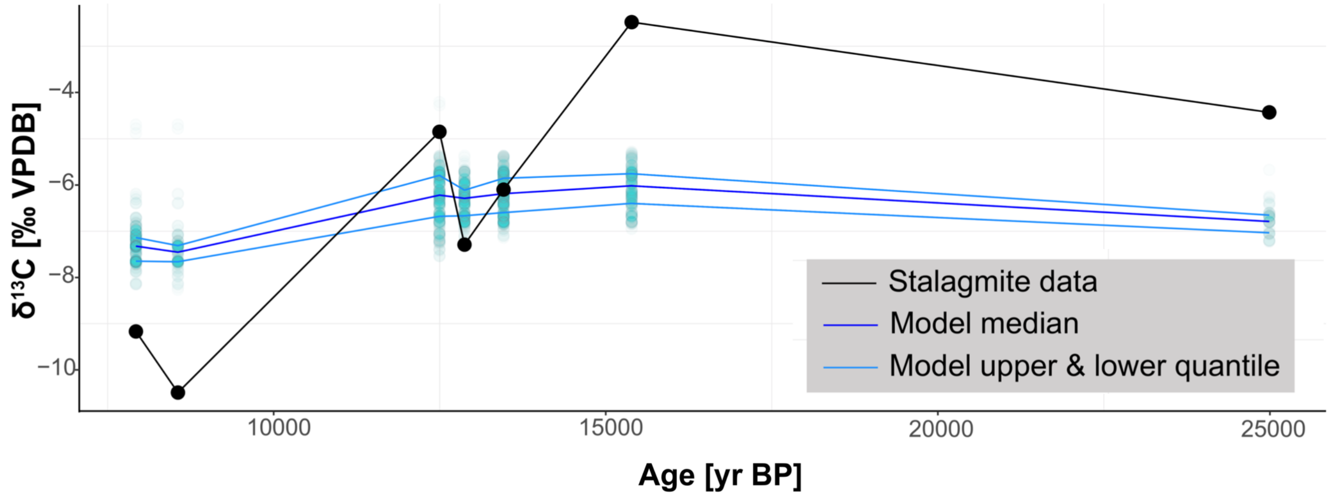
Franziska A. Lechleitner[1,2], Christopher C. Day[1], Micah Wilhelm[3], Negar Haghipour[4,5], Oliver Kost[4], Gideon M. Henderson[1], Heather Stoll[4]

(1) Department of Earth Sciences, University of Oxford, UK (2) Department of Chemistry and Biochemistry, University of Bern, Switzerland (3) Swiss Federal Institute for Forest, Snow and Landscape Research, Switzerland (4) Department of Earth Sciences, ETH Zürich, Switzerland (5) Laboratory for Ion Beam Physics, ETH Zürich, Switzerland

Main Points:

- We use a multi-proxy approach ($\delta^{13}C$, ^{14}C, $\delta^{44}Ca$) and modelling to investigate what causes the large shift (~8‰) in speleothem $\delta^{13}C$ in northern Spain after the last deglaciation
- We find that in-cave and karst processes can only explain part of the $\delta^{13}C$ shift
  - ➢ **changes in soil $\delta^{13}C$ need to be invoked, suggesting a shift in surface vegetation type and/or density occurred**



Introducing the problem | Speleothem Carbon Isotopes | Study site & methods | Results: Geochemistry | Results: Modelling | Discussion & Conclusions

The Problem

- In Western Europe, speleothem δ^{13}C often closely resembles temperature reconstructions (e.g., Genty et al., 2003, Genty et al., 2006, Moreno et al., 2011, Fig. 1).
- The causes for this temperature sensitivity remain poorly constrained, as many processes could be responsible:
    - Vegetation and soil processes
    - Host rock dissolution regime (open vs. closed system)
    - In-cave degassing and carbonate precipitation (incl. prior calcite precipitation)
- **Here, we investigate the relative importance of these processes on δ^{13}C in a stalagmite from Northern Spain as an example for other Western European records (Fig. 1).**

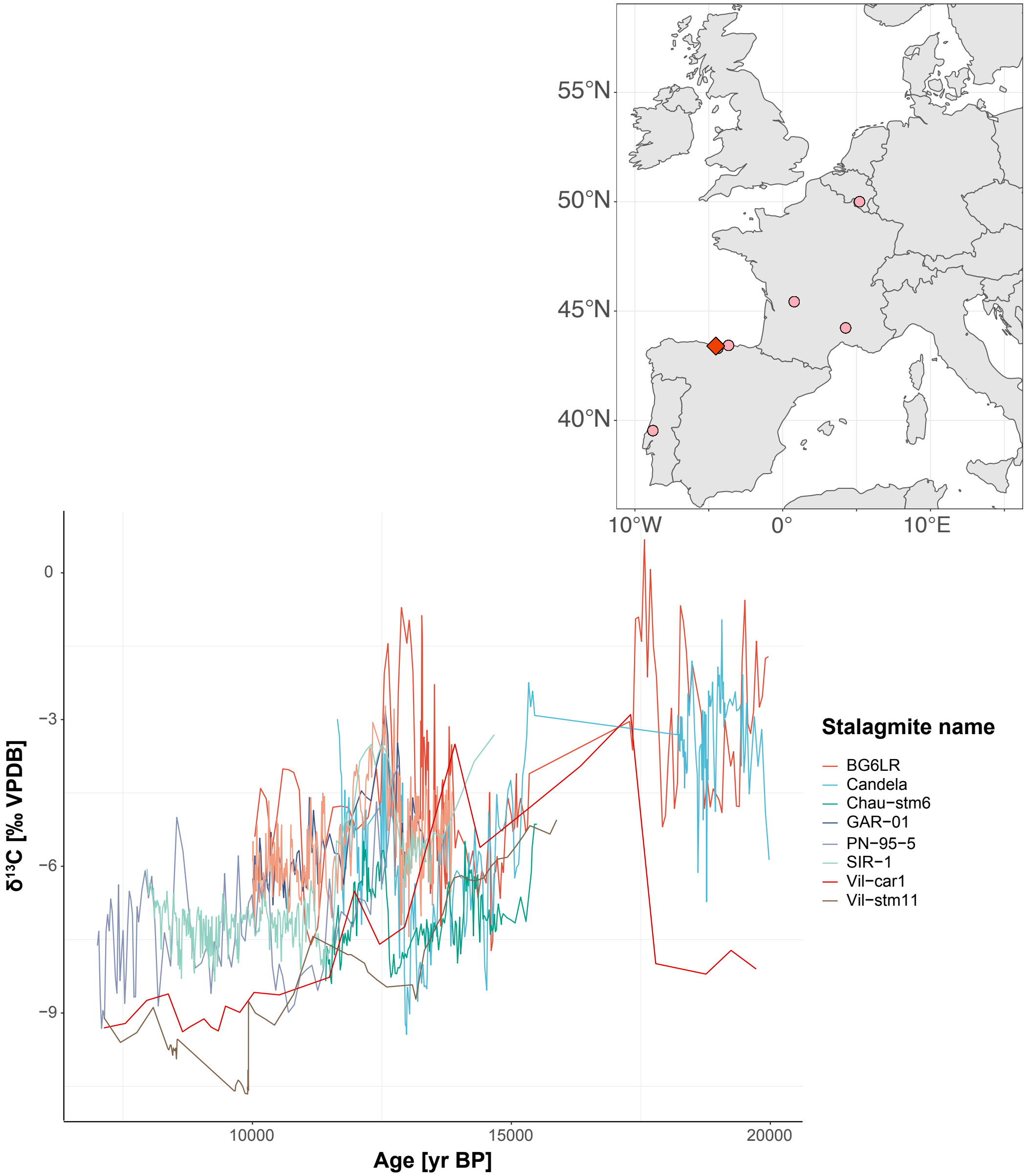
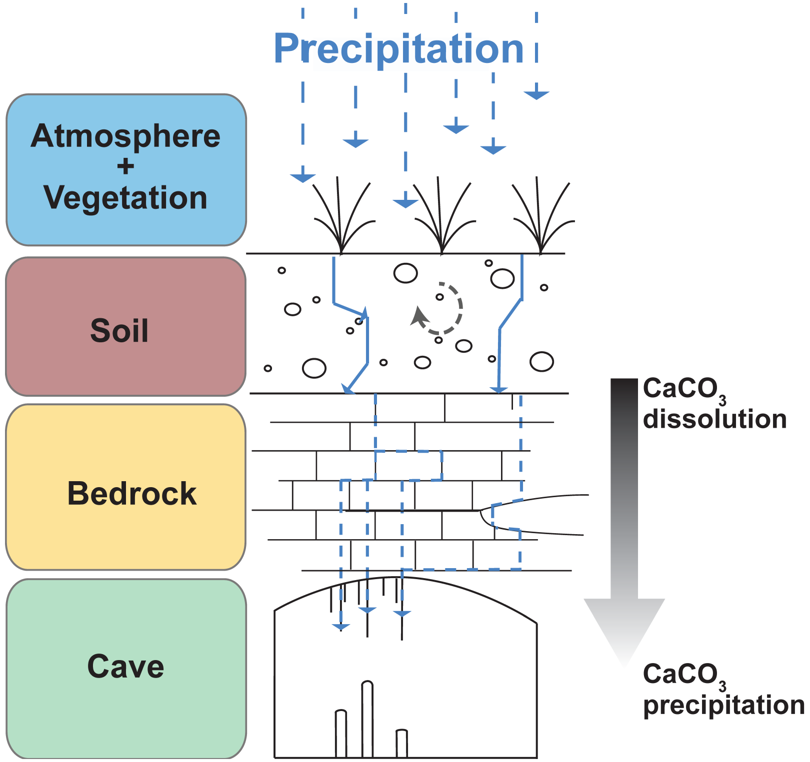


Figure 1: Speleothem records from Western Europe covering the last deglaciation. Data was extracted from the database SISAL (v2, Comas-Bru et al., 2020; references for the individual records are at the end of this presentation).



Adapted from Lechleitner et al., 2016, *GCA*

$\delta^{13}C$	Processes	Ancillary proxy
-8.5 ‰		
-25 - -10 ‰	Vegetation type (C3/C4) Vegetation density Microbial activity (pCO_2) Exchange with atmosphere	
0 ‰	Host rock dissolution (open vs. closed system)	^{14}C – DCP
-20 - -10 ‰	Carbonate precipitation (speleothem and PCP)	Mg/Ca $\delta^{44}Ca$

Ancillary proxies have distinct sensitivity to 1-2 processes

➢ We use them in a soil-karst-cave model to estimate the resulting change in $\delta^{13}C$ from different initial conditions in soil, bedrock, and cave.

Study site:

- Stalagmite Candela from El Pindal cave, northern Spain covers the last deglaciation (25-7 ka BP)
- The site is characterized by temperate climate conditions (MAAT: ~12°C, MAP: ~1250 mm) and is adjacent to the present day coastline
- The cave is covered by a thin soil (0-60 cm), vegetation is composed of sparse shrub pasture and gorse shrub (Rudzka et al., 2011).

Methods:

Geochemistry: Samples for $\delta^{13}C$, ^{14}C, trace elements, and $\delta^{44}Ca$ were taken from the same aliquot of powder, drilled at locations previously sampled for U-Th measurements.

Modelling: Using CaveCalc (Owen et al., 2018), we investigate the sensitivity of the different proxies to processes in soil, karst and cave. The solutions most closely matching the dead carbon fraction (DCF, ^{14}C reservoir effect) and $\delta^{44}Ca$ were selected from a large ensemble of simulations, and the $\delta^{13}C$ from these solutions was compared with the stalagmite (Fig. 2).

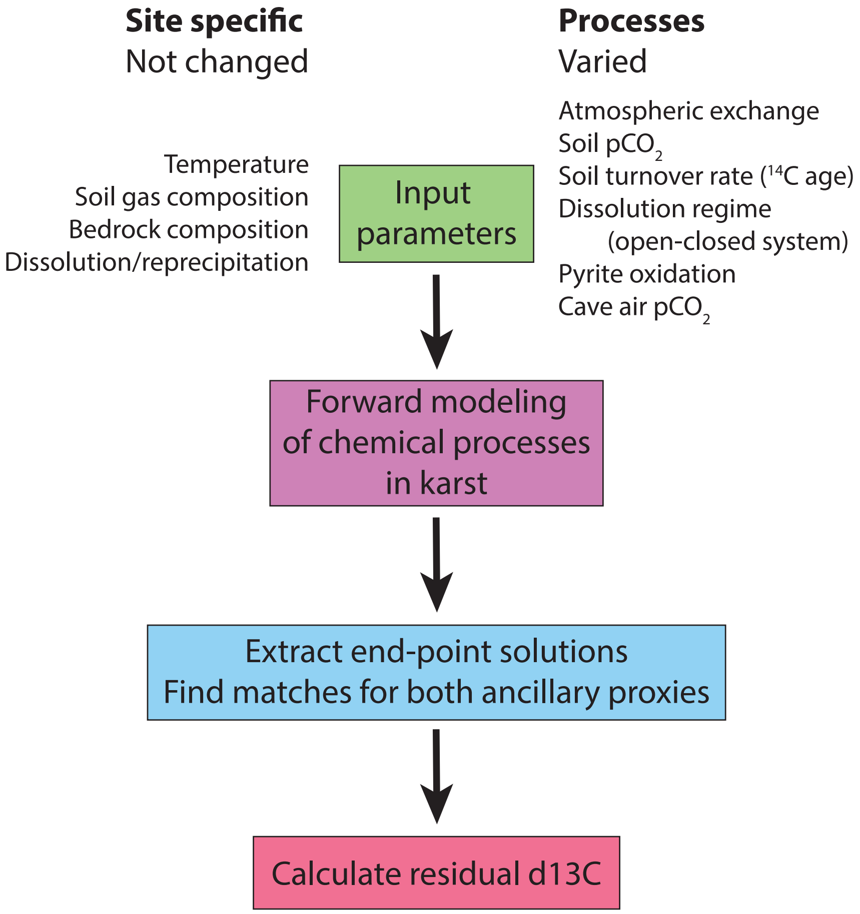


Figure 2: Flowchart detailing the modelling procedure and input parameters.

Study site & Methods

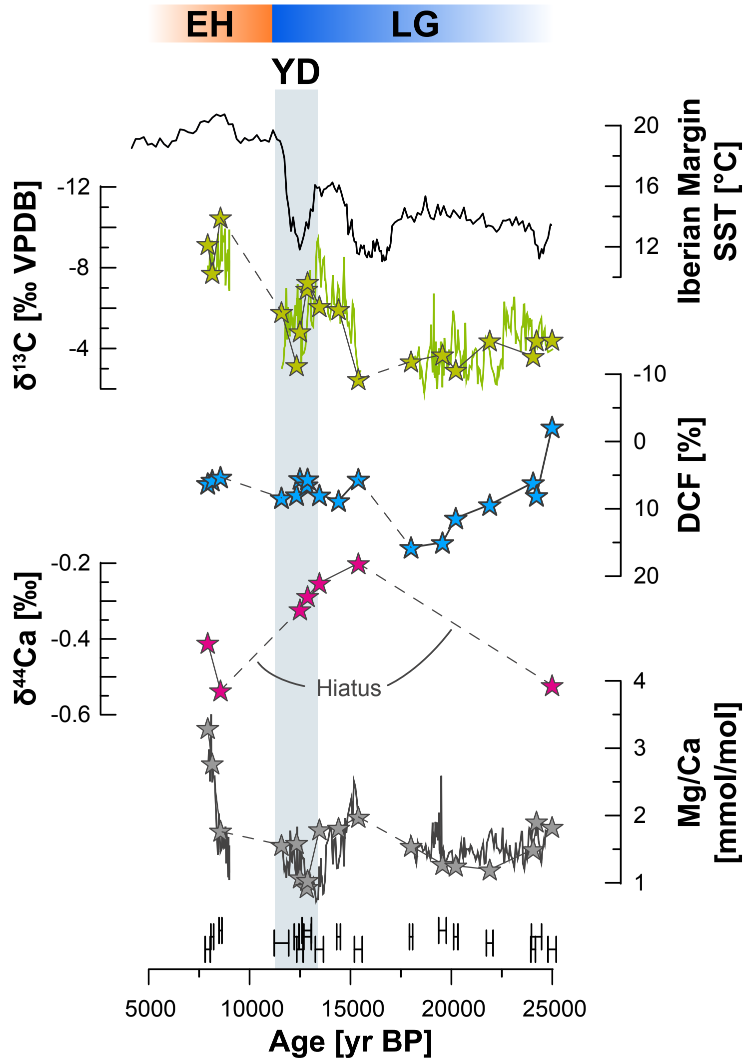


Figure 3: Geochemical records from stalagmite Candela. High resolution $\delta^{13}C$ and Mg/Ca by Moreno et al., 2011. The Iberian Margin sea surface temperature (SST) record is by Darfeuil et al., 2016.

- $\delta^{13}C$ closely follows SST record (Darfeuil et al., 2016, Fig. 3)
- DCF: affected by soil ^{14}C age and addition of ^{14}C-dead host rock carbon
- Mg/Ca and $\delta^{44}Ca$: affected by prior calcite precipitation (PCP)
- Mg/Ca also affected by marine aerosol contribution
  - ➢ $\delta^{44}Ca$ fits a theoretical calcite precipitation trend, thus we use $\delta^{44}Ca$ to evaluate the influence of PCP on $\delta^{13}C$ (Fig. 4)

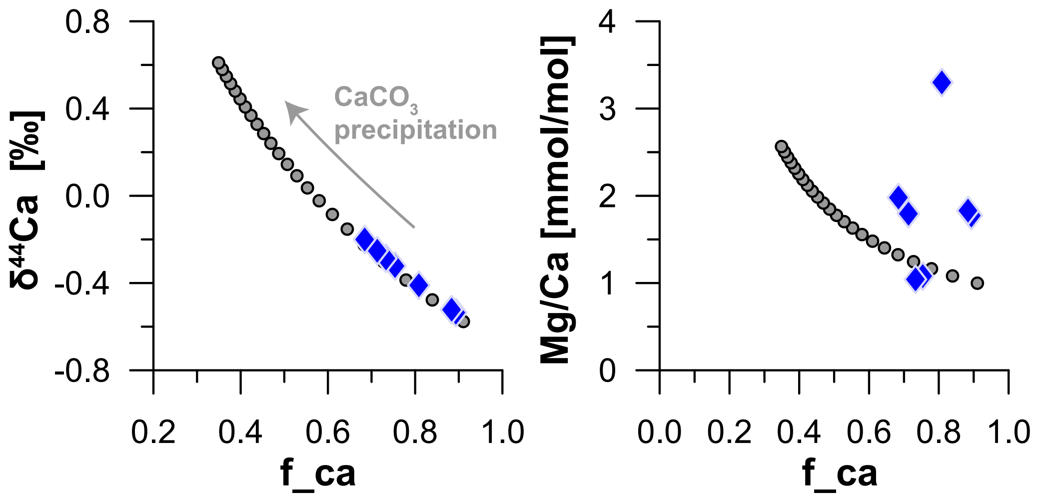


Figure 4: Comparison of stalagmite Mg/Ca and $\delta^{44}Ca$ data to theoretically calculated carbonate precipitation lines (f_ca indicating the amount of $CaCO_3$ that is lost from the solution with increasing precipitation). The excellent match between measured and theoretically predicted $\delta^{44}Ca$ highlights its suitability for PCP reconstruction.

Results: Geochemistry

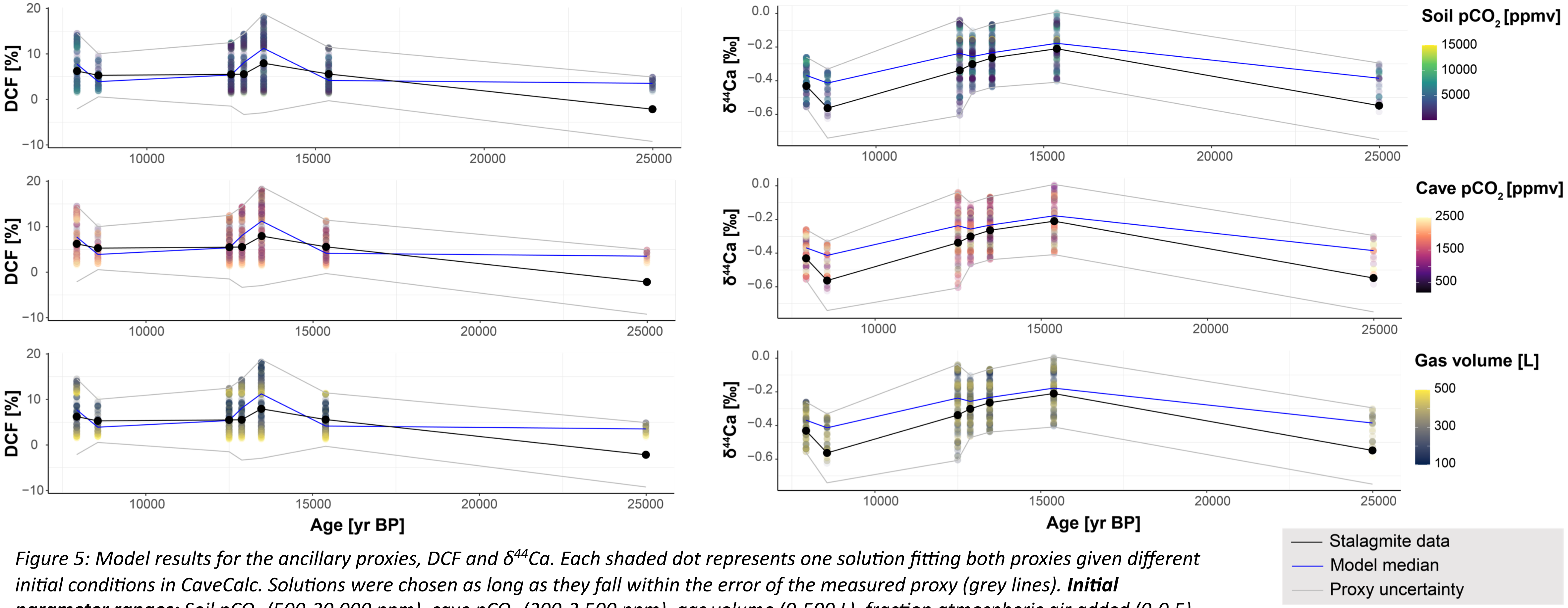


Figure 5: Model results for the ancillary proxies, DCF and $\delta^{44}Ca$. Each shaded dot represents one solution fitting both proxies given different initial conditions in CaveCalc. Solutions were chosen as long as they fall within the error of the measured proxy (grey lines). ***Initial parameter ranges:*** *Soil pCO_2 (500-20,000 ppm), cave pCO_2 (200-2,500 ppm), gas volume (0-500 L), fraction atmospheric air added (0-0.5), soil $F^{14}C$ (80-100 pMC), pyrite added ($0-1x10^{-5}$)*

Ancillary proxies (DCP and $\delta^{44}Ca$) – ca. 10,000 models for early Holocene, 4,000 models for late Glacial: without additional constraints, changes in soil pCO_2, cave pCO_2, and dissolution regime in response to climate are masked by competing effects from different processes.

Results: Modelling

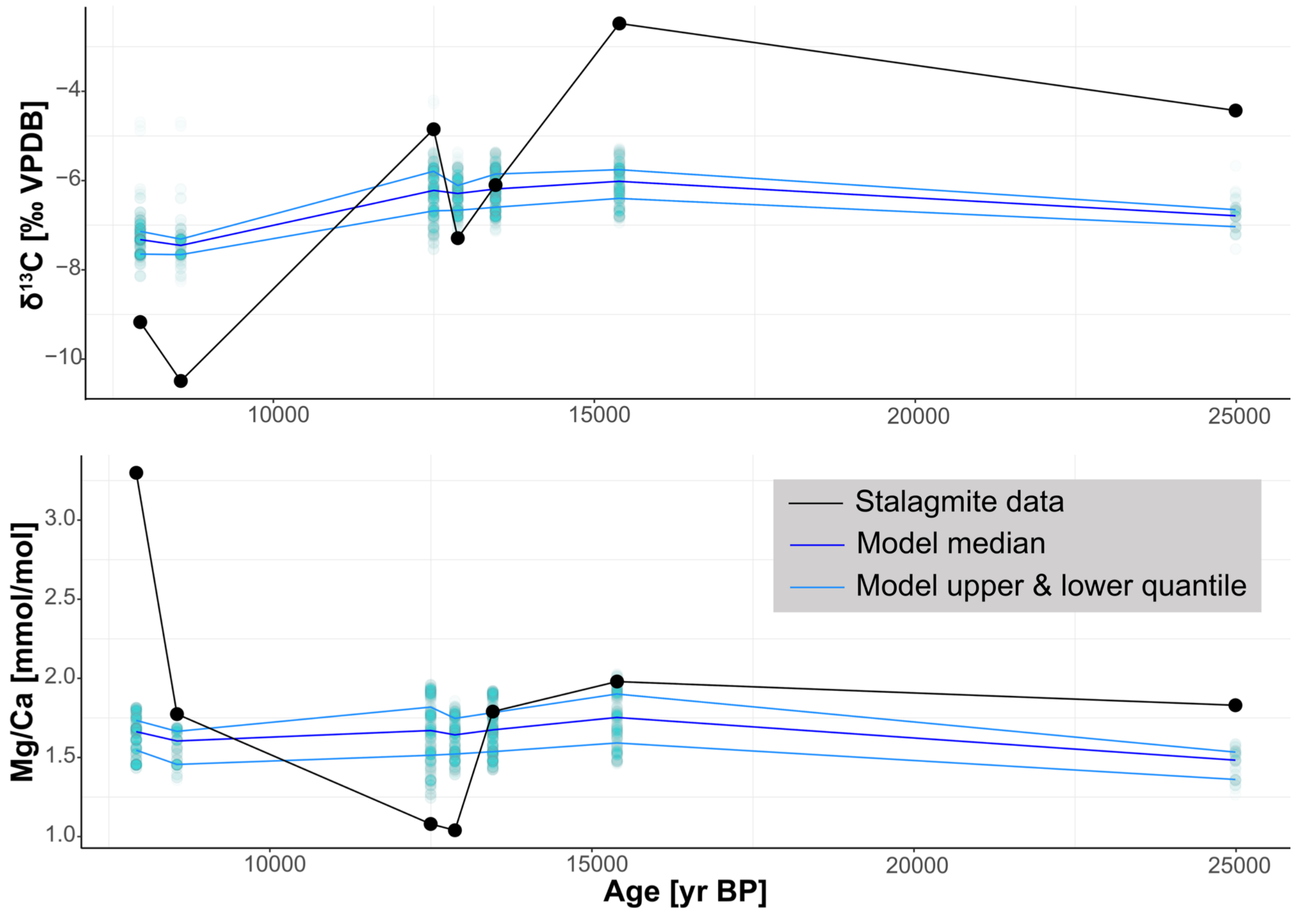


Figure 6: Model results for $\delta^{13}C$ and Mg/Ca. Each dots represents one of the solutions fitting both DCP and $\delta^{44}Ca$.

$\delta^{13}C$ and Mg/Ca values corresponding to ancillary proxy solutions

- For both $\delta^{13}C$ and Mg/Ca, the modelled reconstruction based on DCF and $\delta^{44}Ca$ does not represent the real variability in the proxy.
- Mg/Ca at Pindal cave is affected by marine aerosol contributions (increasing with rising sea level during deglaciation).
- What else affects $\delta^{13}C$? Likely the effect of changes in soil gas $\delta^{13}C$, which in turn is related to vegetation type and density, and exchange between soil gas and atmosphere.

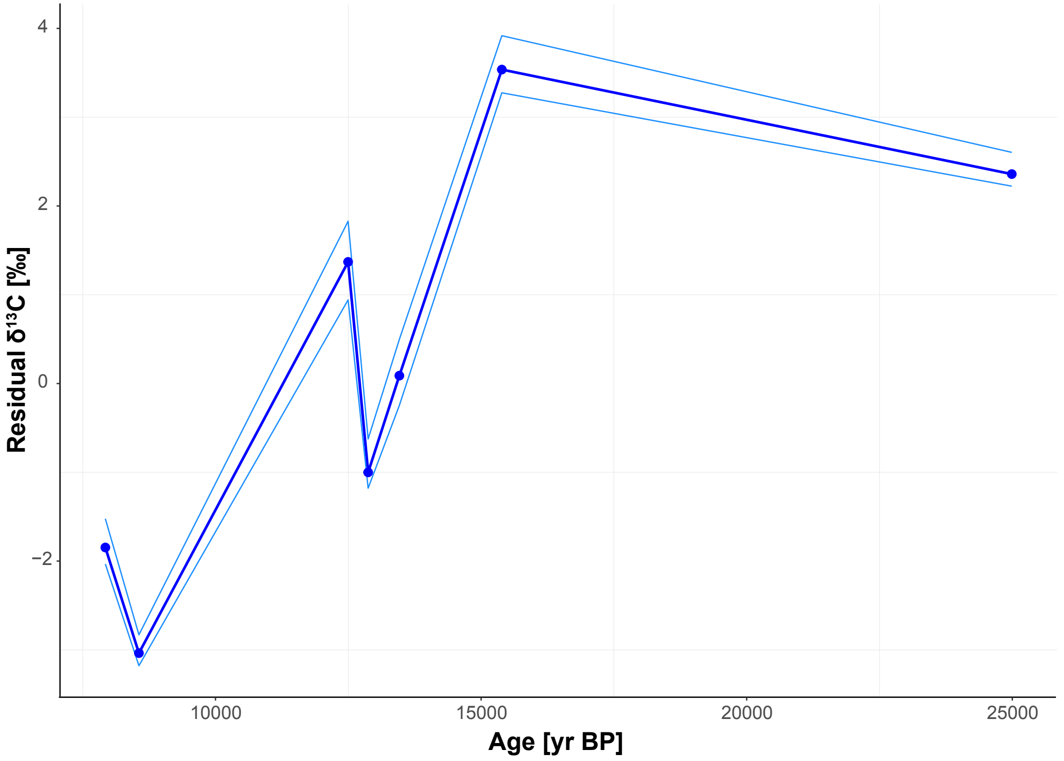


Figure 7: Calculated residual $\delta^{13}C$, i.e., difference between measured proxy value and model median. The upper and lower quantiles are indicated by light blue lines.

- By generating a large ensemble of simulations with differing initial conditions, we can evaluate the importance of karst processes and their combinations on DCF, $\delta^{44}Ca$, $\delta^{13}C$, and Mg/Ca.
- We find that while we can find models matching the DCF and $\delta^{44}Ca$ records, the combination of processes is not trivial to interpret, resulting in no clear signal over the deglaciation (e.g., increasing soil pCO_2).
- Even this large ensemble of models cannot reproduce the decrease in $\delta^{13}C$ found in stalagmite Candela over the deglaciation.
- The decrease in Candela is of similar magnitude to other stalagmite records from Western Europe. **Our results suggest that changes in the soil gas $\delta^{13}C$ are needed in order to explain these shifts. It is likely that these reflect changes in surface vegetation type (grassland vs. forest transition) that occurred with the end of the last ice age.**

Discussion & Conclusions

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References & Acknowledgements