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

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Main Points:

• We use a multi-proxy approach (\(\delta^{13}C, \delta^{14}C, \delta^{44}Ca\)) 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

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Introducing the problem

Speleothem Carbon Isotopes

Study site & methods

Results: Geochemistry

Results: Modelling

Discussion & Conclusions

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[Graph showing change in \(\delta^{13}C\) over time]
• In Western Europe, speleothem δ\textsuperscript{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\textsuperscript{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).
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.

### δ$^{13}C$

- $-8.5\%$ ☐
- $-25 - -10\%$
- $0\%$
- $-20 - -10\%$

### Processes

- Vegetation type (C3/C4)
- Vegetation density
- Microbial activity ($pCO_2$)
- Exchange with atmosphere
- Host rock dissolution (open vs. closed system)
- Carbonate precipitation (speleothem and PCP)

### Ancillary proxy

- *$^{14}C – DCP$*
- *Mg/Ca*
- *$\delta^{44}Ca$*
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).
Results: Geochemistry

- $\delta^{13}C$ 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 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.

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.
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.
\[ \delta^{13}C \text{ and Mg/Ca values corresponding to ancillary proxy solutions} \]

- 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 6: Model results for \( \delta^{13}C \) and Mg/Ca. Each dots represents one of the solutions fitting both DCP and \( \delta^{44}Ca \).
• By generating a large ensemble of simulations with differing initial conditions, we can evaluate the importance of karst processes and their combinations on DCF, δ^{44}Ca, δ^{13}C, and Mg/Ca.
• We find that while we can find models matching the DCF and δ^{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 δ^{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 δ^{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.**

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