

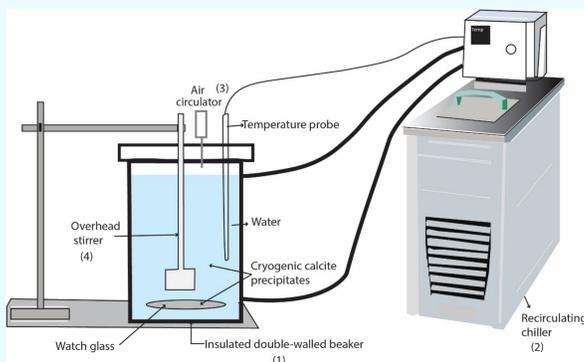


## Introduction

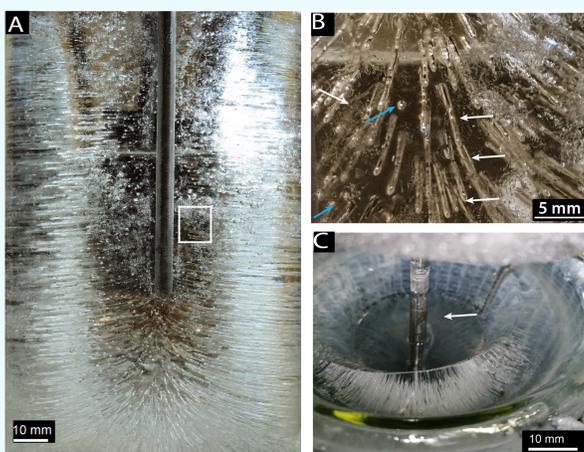
- Cryogenic cave carbonates (CCCs) represents a specific type of **speleothem** formed from freezing water bodies or films in caves (Žák et al., 2004).
- There is a plethora of researches on CCC precipitation kinetics, crystal habit, mineralogy, crystallography and geochemistry.
- Uncertainties remain, as the **cave waters** from which CCC form are not preserved.
- This research aims to (i) report details on experimental **ice formation** and its relation to the **precipitation** of CCCs, to (ii) link CCC **morphotypes** to specific physico-chemical conditions, and to (iii) report the **stable isotopic** composition of CCCs, ice and residual water.

## Methods

- The experiments were performed at **different temperatures** (+1, 0, -0.5, -0.7, -1, and -2 °C) and **durations** between 6 to 91 days.
- We apply gradually cooled, **calcium-rich bicarbonate water** of known isotopic composition to induce CCC precipitation (Fig. 1).
- This study observes how the artificial ice grows (Fig. 2), and explores the **chemistry** of the initial and final water.
- The **morphology** and isotope geochemistry of the corresponding CCC's were studied.

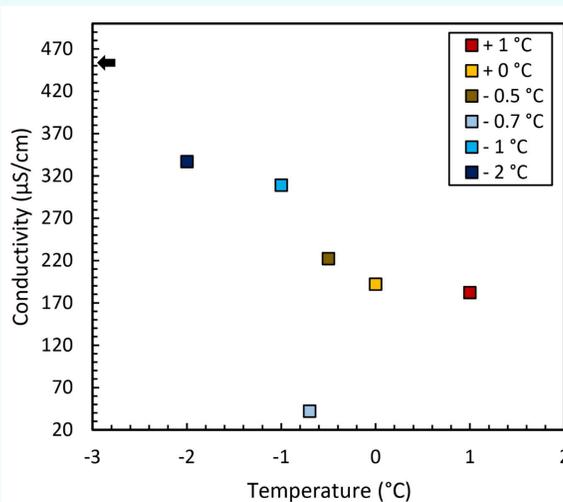


**Figure 1.** Schematic diagram of the experimental setup mimicking natural cryogenic carbonate precipitation.



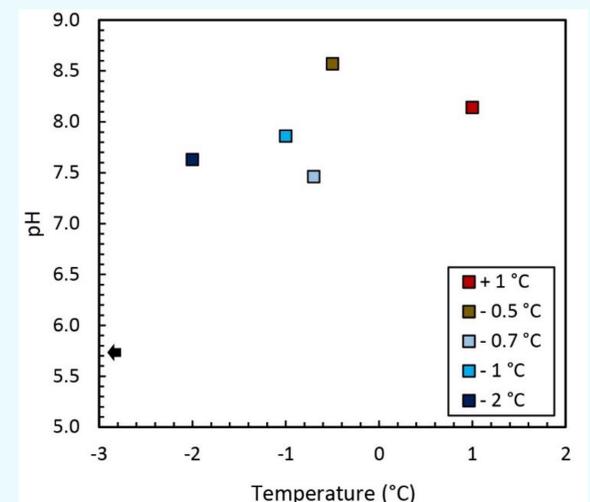
**Figure 2.** (A) Photomicrographs of gas bubble inclusions in the artificial ice resulting from the experiment at temperature (-1 °C). The white and blue arrows in (B) point to the elongate and spherical bubbles respectively. (C) Arrow points to residual water after some aliquots have been taken for analysis.

## Results and Discussion



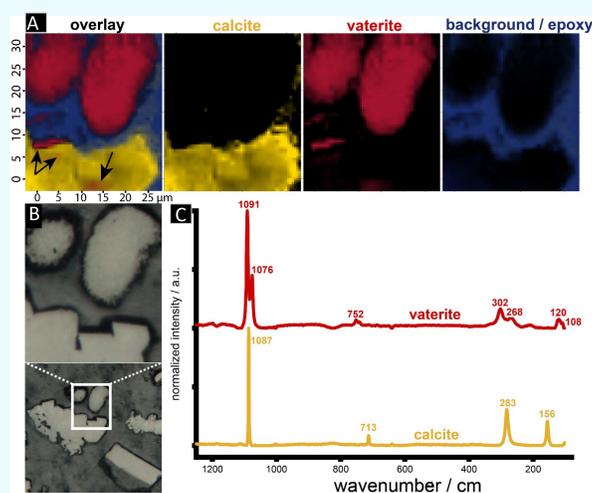
**Figure 3.** Electrical conductivity (EC) plotted against temperature. Black arrow indicate mean initial water composition. Note a decrease in EC due to carbonate precipitation.

- Generally, there is a substantial decrease in the **EC** of the formational water with increasing temperature (Fig. 3).
- The highest amount of precipitated CCC's was observed by at the **lowest EC values**.

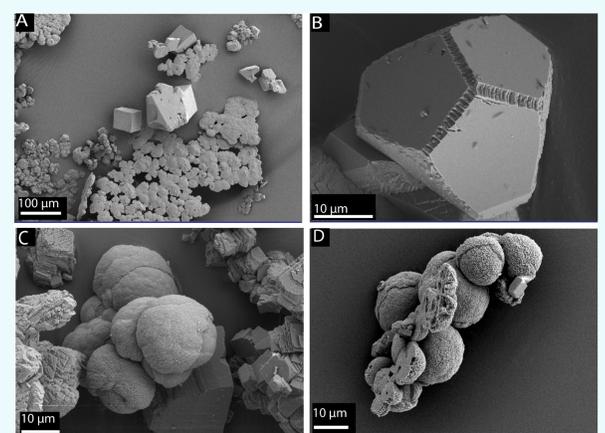


**Figure 4.** pH plotted against temperature. Black arrow indicates mean initial water composition. Note an increase in pH due to CO<sub>2</sub> degassing.

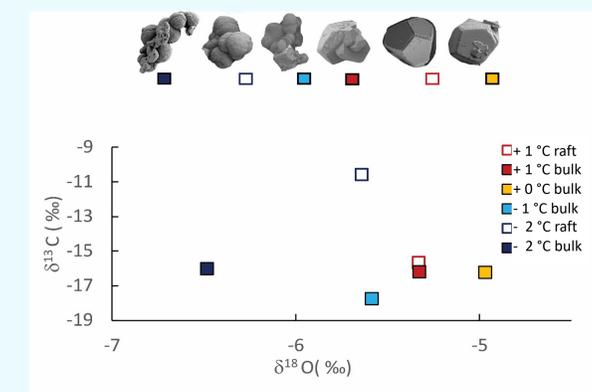
- **pH** value will rise and super saturation with respect to calcite will cause precipitation of CaCO<sub>3</sub> (Fig. 4).
- **CO<sub>2</sub> degassing** will change the species distribution of the DIC towards HCO<sub>3</sub><sup>-</sup>.



**Figure 5.** Raman images of synthetic CCCs. (A) Showing the distribution of two polymorphs vaterite (red) and calcite (yellow). (B) Corresponding bright field image of the region of interest measured in a. (C) Spectral signatures of calcite and vaterite.



**Figure 6.** SEM images of rhombohedral and spherulitic CCCs from experiment (1 and -2 °C). (A-B) Single rhombohedra crystals (C) Spherulite aggregate formed in suspension. (D) Spherulites formed in suspension.



**Figure 7.** Carbon and oxygen isotope value of the synthesized CCC. Carbonates include rafts and bulk CCC's.

- The rafts show **higher δ<sup>13</sup>C** values than the bulk crystals (Fig. 6).
- Correlating isotopic composition with morphology, the **rhombohedron** form first, followed by the **spherulites**. This precipitation trend agrees with previous studies (Žák et al., 2018; Töchterle et al., 2022).

## Conclusions

- Subtle differences in **water temperature and calcite saturation index** has a significant impact on CCC morphology.
- The **Spherulites (vaterites)** form only when the water is **completely frozen**. In contrast, the **rhombohedral** crystals occur in experiments with or without ice formation.
- Conductivity, pH, rate of freezing also influence the morphological type. Higher water saturation leads to the formation of the **spherulites** which form at the later stage.
- **Laboratory experiments** as documented here provide an opportunity to test and improve hypotheses based on empirical studies of natural CCC occurrences.
- Eventually, this will advance our understanding of this intriguing **carbonate archive** and allow for a more **robust** interpretation of their proxy data.

## Contact

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## References

Töchterle, P., Steidle, S., Edwards, R. L., Dublyansky, Y., Spötl, C., Li, X., ... & Moseley, G. E. (2022). <sup>230</sup>Th/U Isochron Dating of Cryogenic Cave Carbonates. *Geochronology Discussions*, 1-16.  
Žák, K., Onac, B. P., Kadebskaya, O. I., Filippi, M., Dublyansky, Y., & Luetscher, M. (2018). Cryogenic mineral formation in caves. In *Ice caves*. Elsevier. 123-162  
Žák, K., Urban, J., Čilek, V., & Hercman, H. (2004). Cryogenic cave calcite from several Central European caves: Age, carbon and oxygen isotopes and a genetic model. *Chemical Geology*, 206, 119–136.