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Comment on cp-2021-86

Anonymous Referee #1

Referee comment on "Last glacial millennial-scale hydro-climate and temperature changes in Puerto Rico constrained by speleothem fluid inclusion $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values" by Sophie F. Warken et al., Clim. Past Discuss., <https://doi.org/10.5194/cp-2021-86-RC1>, 2021

The authors present new fluid inclusion isotope data for an exceptionally well dated stalagmite that had been studied for carbonate stable isotope and trace element compositions by Warken et al. (2020). They convincingly separate fluid inclusion $\delta^2\text{H}$ and $\delta^{18}\text{O}$ data affected by evaporation and discuss paleotemperatures obtained from samples which are thought to contain primary, unaltered water and calcite oxygen isotope compositions. The paper is well written, concise enough and easy to follow. The new data are valuable and worth to publish.

However, I see two main problems with the data.

1) The evaporation process. The inclusion data clearly reflect evaporation. Evaporation may occur in the atmosphere and on the surface. In this case the precipitating calcite can reflect the shifted water $\delta^{18}\text{O}$ value, provided that increasing evaporation is not associated with increasing temperature, whose fractionation effect can counteract the evaporation related isotope shift, leading to constant $\delta^{18}\text{O}$ in the calcite. The present study suggests cold and dry conditions, in which case the positive $\delta^{18}\text{O}$ change in the water would be enhanced in the calcite due to the elevated calcite-water oxygen isotope fractionation, which is obviously not the case.

Another possibility is evaporation along the karstic water migration route. In this case evaporation would also be associated with enhanced CO_2 degassing and strong PCP. Warken et al. (2020) excludes this possibility as the Sr/Ca ratios are not changing along with the Mg/Ca values. Additionally, the water arriving at the stalagmite surface would already be evaporated and its isotope compositions would be shifted, that should appear in the calcite.

The next possibility is evaporation on the stalagmite surface and this is what the authors suggest as a potential process. However, it is difficult to imagine that calcite is precipitated from an unaffected solution, then the water film is evaporated, and the calcite

precipitating from the evaporated water would not show any $\delta^{18}\text{O}$ shift. Further, the low H_2O contents should be associated with higher $\delta^{13}\text{C}$ values in the calcite. I tried to plot the water contents on the $\delta^{13}\text{C}$ record presented by Warken et al (2020), and the relationship is not convincing.

I plotted the data and it is apparent that the water content and the fluid inclusion $\delta^2\text{H}$ and $\delta^{18}\text{O}$ data are negatively correlated (with r^2 values around 0.32 for logarithmic fitting). However, it is not clear why the evaporation from the water film on the surface would result in lower amount of fluid inclusions in the calcite. Evaporation should increase the calcite saturation, leading to faster carbonate precipitation and more inclusions trapped.

An alternative process is partial leaking of inclusions. As the sample chips were held in a carrier gas flow, they were most probably heated to remove the adsorptively bound water. Although this is not mentioned exactly, the authors mention 120 °C in the vacuum line to avoid water condensation. Heating speleothems to 120 °C may partially open large inclusions. The changes in climate conditions may change the carbonate fabric, inclusion entrapment, and hence the tendency of inclusion leakage during heating, as well. Partial removal of inclusion-hosted water due to inclusion leaking may lead to lower water content and shifted isotope compositions. This process is also supported by the large variations in water contents and isotopic compositions in the same sample (e.g. sample 24).

Heating the samples at different temperatures (80, 100, 120 °C) in a vacuum system and record the vacuum achieved, or measuring pieces from the strongly evaporated laminae at lower temperature (e.g., 80 °C) would provide means to investigate this potential measurement bias. Additionally, calcite and fluid inclusion petrography is essential in order to see if there is any fabric and textural change related to changes in climate conditions.

Further, the fluid inclusion data should be compared with the averaged $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Mg/Ca values in order to see if these evaporation- and degassing-sensitive proxy data are affected. Enhanced cave ventilation is mentioned in line 372 that should be supported by $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ correlation.

2) Paleotemperature uncertainty. The paleotemperature data are valuable, but their scatter is too high to discuss <2 °C differences between different periods. The authors state that the interstadial values are 1.6 °C higher than the MIS3 average. However, the interstadial average contains data from sample 24, which is very inhomogeneous. As the authors mention, some of the data were excluded from the calculations due to the evaporation affect, and the temperatures are taken as maximum values. However, if some periods are affected, and some others are not (due to carbonate texture differences), then the uncertainty becomes much higher than the 1.6 °C difference.

The authors state that the 22.0 ± 1.8 °C temperature for the interstadial periods is comparable with the present day condition. However, the former is obtained from

inclusion data, the latter is from direct temperature measurement. I know that it is not a nice suggestion to collect more samples from Puerto Rico, but if the authors accidentally have modern samples or at least Holocene stalagmites, only some measurements may strengthen this statement.

Additional comments:

line 155: „Sections with a relatively high water content, e.g., around c. 28 or 34ka...“. The water content at 34 ka is low, as far as I see.

line 194: It would be informative to plot curves of the Johnston et al. (2013) equation for different temperatures in Fig. 4a.

line 295: „Post-depositional enrichment of ^{18}O in fluid inclusion water due to evaporation“. Post-depositional but pre-entrapment?

line 302: In order to support this sentence, the fluid inclusion data and the proxy records should not only be plotted together, but a statistical analysis between these variables (with the high-resolution proxy data averaged for the inclusion sampling) is suggested.

line 332: „a drier state and weak convection“. If the reliable flint temperatures are plotted together with the Mg/Ca record of Warken et al 2020, there seems to be a positive relationship that supports the assumptions presented here.

line 358: „The pattern largely follows the evolution of the high-resolution calcite stable isotope record (Fig. 2).“ Looking at Fig. 2, this is rather risky to state. I made a linear correlation between the inclusion data and the averaged $\delta^{18}\text{O}_{\text{cc}}$ values, there is no statistically supported correlation.

