

Clim. Past Discuss., referee comment RC2
<https://doi.org/10.5194/cp-2021-86-RC2>, 2021
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Comment on cp-2021-86

Anonymous Referee #2

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-RC2>, 2021

This manuscript presents a study of fluid inclusion isotope composition from a speleothem sampled in a cave from Puerto Rico, which today experiences seasonal ventilation variations. The data in this paper are high quality fluid inclusion dD and d18O measurements covering the 46-15 ka period made using state of the art methodology. The excellent team of authors show that the FI data can be grouped into two distinct d18O-dD groups. One group falls on the global and local meteoric water lines. This group represents samples with FI yields greater than 0.55 microliter/g. The second group, characterized by FI yields less than 0.55 microliter/g shows a strong deviation from the local meteoric water line in an apparent evaporation trend characterized by a dD/d18O slope significantly lower than that of the meteoric water line. The calcite of the former group is proposed to form at, or near, temperature d18O equilibrium with the fluid inclusion water. The calcite d18O of the second group is similar in range to the first group, and consequently is in isotopic disequilibrium with the FI waters of the second group. The controls of the proposed evaporation process are climatic-driven ventilation during colder periods. Thus, the first group of FI waters and calcites are considered to reflect high cave humidity warm period conditions, whereas the evaporated samples reflect colder periods characterized by enhanced cave ventilation.

The kinetic mechanism proposed to account for these contrasting modes is very interesting. The speleothem calcite precipitates rapidly in both warm and cold periods in or near temperature isotopic equilibrium with cave drip waters. In the colder periods characterized by enhanced ventilation, evaporation of the dripwater films and the fluid inclusions trapping these evaporated waters occurs, yielding the deviations observed from the meteoric water line. However, the kinetics of the calcite-bicarbonate exchange is so slow that the speleothem calcite does not reset to the evaporated water values: the calcite thus retains the original 'equilibrium precipitation signature' attained prior to the onset of evaporation driven d18O changes. The model is well explained and the findings of the paper are both interesting and innovative.

This is an intriguing experimental data set, well-written, innovative in scope, and the manuscript certainly deserves publication. Nevertheless, there are several points that I

would like to see addressed before the manuscript becomes published.

- What is the advantage of using the Johnson et al (2013) thermometer calibration over the more generally used Tremaine et al (2011) calibration. The Tremaine et al calibration has become something of a standard in cave thermometry.
- I have some reservation over the explanation of the proposed evaporation trend. The shift of d18O from the meteoric water line value is as much as 12 permil. This is a huge evaporation effect! The authors should use a Rayleigh calculation to estimate fraction of the original water that has evaporated away before leaving the residual water in the fluid inclusions of the evaporated samples. I would guess that the amount of residual water in the fluid inclusion is a small fraction of the calculated original water amount, and that the calculated original water amount is much higher than the water present in the first group samples, which contain about 0.5-2 microliter/g. The authors should explain how their proposed mechanism of fluid inclusion entrapment is compatible with high degrees of evaporation. Is there any alternative mechanism that could account for the apparent evaporation trend e.g, a process during analytical handling?
- There is no graph of calculated temperature vs age showing the variations with time. I think that such a graph should be added to the paper. This graph could show the disequilibrium temperatures of the second group as well the "good" temperatures of the first group. Also, I am not completely clear how the authors calculated temperatures for the cold period samples. Did they use the water d18O value given by the intersection of the evaporation and meteoric water lines (Fig 3b)? If so, I would point out that one could run several different evaporation lines through the data. As Fig 3b shows, the evaporation line they calculated averages out quite widely disperse data.