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Climate of the Past Discussions

Interactive comment on "Experimental evaluation of oxygen isotopic exchange between inclusion water and host calcite in speleothems" *by* Ryu Uemura et al.

Anonymous Referee #2

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This contribution by Uemura et al. presents a series of experiment concerning the diagenetic alteration of fluid inclusion water in speleothem (stalagmite) calcite.

Over the past decades, fluid inclusion oxygen and hydrogen isotope analysis has become accepted to be a very useful addition to the toolbox of geochemical proxies applied on speleothem (stalagmite) climate archives. As stalagmite fluid inclusion isotope data are believed to represent the isotope composition of rainwater back in time, they potentially provide the warm-climate equivalent of the famous Ice Core isotope records. There are complications, however. One major issue is the potential post-depositional oxygen isotope exchange between the fluid inclusion water and host calcite, that cause

the fluid inclusion isotope measurement to represent a diagenetic, rather than a rainwater d18O value. Uemura et al. study this process by heating stalagmite material to 105 degrees C, in an attempt to force diagenetic (thermal) alteration of fluid inclusion water. Their results show that such alteration takes place, but has a rather limited effect on the d18O value of the fluid inclusions only. It is demonstrated how this likely reflects isotope exchange with a very thin layer of CaCO3 around each fluid inclusion. Extrapolation of these results to reasonable natural (glacial-interglacial) variation in temperature that stalagmites are exposed to, suggest that the effects of such limited temperature change on diagenetic alteration of the fluid inclusion water is negligible.

In summary, I believe this is an interesting experiment that gives, for the first time, quantitative insight in the extent of diagenetic alteration of fluid inclusions. The results line up well with several published fluid inclusion stable isotope records that indicate that such diagenetic alteration is not a common process in stalagmites. The ms is well-written, and the experimental results logically explained.

I could phrase some possible criticism on the experiment concerning the following aspects of the studied material and experimental set up:

1) I find no age model of the studied stalagmite, so that it is unclear this this is submodern or ancient material (or anything in between). Not having the ages leaves some uncertainty to what extent the fluid inclusion isotope data should coincide with the meteoric waterline presented in the ms.

2) If I read the ms correctly the high temperature experiment is not performed on samples of the same age (layer) as the low temperature experiment. It would perhaps have been more elegant if that would have been the case. This is by no means a fatal problem since the significant isotope shift through heating takes place in samples that are from a single layer, so the central outcome of this study is fully supported by the data anyhow.

3) What strikes me in the low temperature d2H d18O cross plot is that while the au-

thors state the data to lie between the winter and summer meteoric water lines, the supposedly original fluid inclusion isotope values seem somewhat biased towards the winter rainfall composition to me. If I'm correct, this could have several reasons: 1 Winter rainfall dominating cave recharge at this site. 2 a small isotope artefact in the fluid inclusion isotope data 3 the calculated seasonal meteoric water lines are based on data from another island, and thus may not be entirely representative for the study site. 4 The stalagmite could be somewhat older, and precipitated under a different from modern rainfall regime.

While I'd be interested to hear if the authors agree with my observation, I realize that this latter point can probably not be clarified because not all the information on study site and cave environment (particularly drip water isotope ratios?) are available. I think it is fair to say that such detailed considerations are beyond the scope of the present study. Bottom line is that in this study Uemura et al show clearly to which extent heating experiments are able to affect the isotope ratios of fluid inclusions in stalagmite calcite. I believe this improves our insight in the potential of fluid inclusion isotope analysis in stalagmite records, and thus provides a valuable contribution to the rapidly developing field of speleothem climate science.

Some more detailed comments: 1) Your statement in line 77-79 may require a reference. 2) Where you describe the reproducibility of the fluid inclusion isotope analysis it is not clear what this is based on. Repeated analyses of water samples? replicate analyses of fluid inclusion water? please specify. 3) similar question for the Gasbench isotope analyses. Are the reported uncertainties the sample-internal standard deviations, or based on longer series of carbonate standards? 4)in line 175 you claim that isotopic exchange results in lower d-excess values. Technically speaking this is only the case if the exchange takes place at higher temperatures than the original precipitation temperature. This could essentially go the other way around as well, so it is not exclusively the lower d-excess values that could be indicative for oxygen isotope exchange. Rather, any deviation from the MWL could potentially signal oxygen isotope

exchange under changing temperatures.

I found no further flaws or technical details that must be changed. I therefore would suggest that this can be published with just a few minor (technical) corrections.

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