

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

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Received and published: 18 October 2019

Response to anonymous Referee #1 We thank the anonymous Referee #1 for the detailed and constructive comments. Below, we respond to the comments in order (Referee’s comments are marked with “[#R1-x]”. Our responses are marked with “**”).

[#R1-1] “General comments: The paper experimentally investigates the post-depositional oxygen isotope exchange of fluid inclusion water. As an increasing number of laboratories are developing and applying techniques for fluid inclusion analysis, a sound understanding of the related isotope signals and potential limitations is urgently needed. The constraints provided by this study are therefore very valuable and show

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that in most cases also the fluid inclusion $\delta^{18}\text{O}$ signal may reflect the drip water at time of enclosure. The paper is well structured and written. The used technique is clearly described, all necessary data for discussion are given, and the interpretation is based on the authors' genuine data. The topic is well within the scope of Climate of the Past as it addresses an emerging proxy with high paleoclimatic significance.”

*We appreciate hearing your positive view of our manuscript.

[#R1-2] “Specific comments: Introduction: -line 36-37: Cave dripwaters. . . usually close to the d^{18}O of local rain. Is it? Or is it close to the infiltration-weighted mean of the rain? A literature reference may be sufficient (e.g., Baker et al., 2019, Nat. Commun.)”

*Corrected. We also added the reference you suggested.

[#R1-3] ‘-line 42: . . . suggests a relatively stable value for the temperature dependence of $\text{d}^{18}\text{O}_{\text{ca}}$. . . I would be a bit more cautious here. Mühlinghaus et al. (2009) found that the change of the calcite $\delta^{18}\text{O}$ with temperature has a certain relation to the drip interval which is expressed differently at different cave temperatures. It is relatively limited at 10degC (-0.22 to -0.26 ‰), but quite substantial at 25degC (-0.21 to -0.35 ‰) for the modelled drip intervals.”

* We think that our expression “relatively stable” is too ambiguous. We intended to say the temperature reconstruction is possible. In fact, Mühlinghaus et al. (2009) wrote: “With increasing drip interval the temperature dependence changes due to the buffering and mixing processes but is always within the range of -0.20 and $-0.34\text{‰}^{\circ}\text{C}$. This implies that the interpretation of d^{18}O variations in terms of temperature is still possible for stalagmites grown under conditions of isotopic disequilibrium, if the stalagmite was fed by a relatively constant drip rate.” Of course, the slope is not perfectly constant but still possible with uncertainties. In order to clarify the meaning, we removed the expression “relatively stable”. Instead, we added exact values of the slope (-0.20 and $-0.34\text{permil}/^{\circ}\text{C}$) in the sentence.

[#R1-4] “Methods -section 2.1: Did you take the speleothem samples for fluid inclusions at the growth axis or off-axis? The position relative to the axis may have an influence on the water content and may also be interesting for the discussion section and Fig.3.”

*We took the samples from the growth axis. Then, a fan shaped sub-sample was symmetrically divided into 3-6 pieces. Thus, the position does not matter. A schematic illustration will be added to explain the shape of sample in Figure 1 (please also refer to [#R1-9]).

[Please refer to the Supplemental PDF for the cut out of revised version of Fig.1]

[#R1-5] “Results and discussion: -lines 137-138: you state that the observed increase is due to exchange between inclusion water and calcite. Could calcite dissolution or new calcite precipitation related to a change in the saturation state following the increased temperature also play a role?”

* We think that dissolution or new calcite precipitation in fluid inclusions could play a role. It is, however, difficult to estimate such effects because it depends on pH and the amount of CO₂ in inclusions. In the case of our experiment, the new calcite precipitation did not occur in the inclusions because the $\delta^{18}\text{O}$ value of water is expected to be lower if the new calcite, whose $\delta^{18}\text{O}$ value is higher than that of water, formed inside the inclusions. This is opposite to the result of heating experiment. In the case of internal calcite dissolution, the $\delta^{18}\text{O}$ value of water, will be changed through the isotopic exchange reaction between the bicarbonate in the solution and the water reservoir. Thus, essentially, it would not differ from the case of re-equilibration between calcite and water. We will add sentences about these possibilities in the revised MS.

[#R1-6] “-lines 144-145: Leakage may also be influenced by the fabric of the stalagmite and be different in inclusions with e.g., large columnar crystals compared to dendritic parts. What is the fabric of the investigated pieces of HSN1? Also the following statements in lines 148-152 should be rephrased considering potentially different behavior of stalagmites with different fabric and micro-structure. Lacking larger data sets of var-

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ious stalagmites, I would be hesitant to generalize. Still the statements are ok for the analyzed sample but should be written in a way that a generalization for the leakage aspect is avoided. “

*Yes, the characteristics of leakage would be different for the different stalagmites. We revised the sentences to describe the potentially different behavior of stalagmites with different fabric and micro-structure in Section 3.2. A description about the fabric of HSN1, open columnar structure, was also added in Section 2.1 “Speleothem samples”.

[#R1-7] “-lines 168-176: is the deuterium excess indeed a (better) indicator for oxygen isotope exchange compared to the closeness to the LMWL?”

*The d-excess is equivalent to the “closeness to the LMWL” when the slope of LMWL is close to 8. We think that the d-excess has advantage of being quantitative (i.e., easy to show the difference with numbers). In addition, we think that this sentence is misleading because logically the opposite direction (higher d-excess) may occur (please also refer to [#R2-8]). Thus, we deleted this sentence and will revise it as follows. “We should note that the d-excess value could become higher if the exchange takes place at lower temperatures than the original precipitation temperature. Therefore, the oxygen isotope exchange under changing temperatures may cause any slight deviation from the LMWL.”

[#R1-8] “-lines 213-215: This sentence may be misunderstood and should be slightly rephrased. Whereas the rate constant of the isotope exchange reaction only varies with temperature, the number of transferred isotopes varies with the temporal evolution of the isotope ratios of the end members.”

* The sentence was rephrased.

[#R1-9] “Fig.1: Please indicate in the figure where the samples were taken for the analysis.”

* We will add the positions of the samples and shape of subsample in Figure 1 (please

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also refer to [#R1-4]).

[#R1-10] "Fig.4: Do you have $\delta^{18}\text{O}$ and δD values of modern drip water from the cave? Or could you alternatively calculate the infiltration-weighted mean of the rainfall? It may illustrate additionally the shift between the 105°C samples and the room-temperature reference that should be close to the dripwater."

*The modern dripwater data will be added to Fig. 4. The HSN1 stalagmite is mid-Holocene sample (6429±55 and 7092±48 years BP) (please also refer to [#R2-2]). Thus, the rain water isotope ratio is likely different from modern rainfall (please also refer to [#R2-4]).

[#R1-11] "Typos: -line 60: "These data suggest *an* isotopic exchange of . . ." or just without the current "the" -line 131: ". . .of inclusion water *are* shown as deviation from . . ."-lines 141-142: either "there is little hydrogen in the calcite" or "there is no significant hydrogen reservoir in the calcite"

* Corrected. We thank you again for your comments and suggestions.

Please also note the supplement to this comment:

<https://www.clim-past-discuss.net/cp-2019-79/cp-2019-79-AC1-supplement.pdf>

Interactive comment on Clim. Past Discuss., <https://doi.org/10.5194/cp-2019-79>, 2019.

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