

Interactive comment on “Climatic variations during the Holocene inferred from radiocarbon and stable carbon isotopes in a high-alpine cave” by Caroline Welte et al.

Anonymous Referee #1

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Summary: Carbon isotopes of speleothems are difficult to interpret because of the several mechanisms that can affect them (changes of plants above the cave, carbonate dissolution mechanisms, in-cave fractionation processes). This study uses a recently developed method of laser ablation coupled to accelerator mass spectrometer to measure high-resolution ^{14}C in a speleothem from western Austria and compares it with stable carbon and oxygen isotopes to explore key processes influencing carbon isotope compositions.

Key findings that I took away from this study: The coupled methodology (novel ^{14}C measurements w/ stable isotopes) reveals changes of the presence of older OM reser-

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voirs in the karst rock above the cave through time that are attributing to changing carbon isotope signals:

1. >8ka: there is an older reservoir of OM that causes low $\delta^{13}\text{C}$ and high dcf. *This interpretation wouldn't have been possible without the ^{14}C measurements because low values of $\delta^{13}\text{C}$ alone lead to the interpretation of C3 vegetation above the cave. . . and the measured high dcf is needed to distinguish this from the actual mechanism of vegetation + an older OM reservoirs source that is causing elevated CO_2 values.

2. 3.8-8ka: There is strong $\delta^{13}\text{C}$ variability and lower dcf. This suggests there is not an older source of OM contributing to the carbon isotope signal, and the interpretation is made it was stabilized/exhausted because of reduced precipitation. While this interpretation makes sense, I do not think bringing in growth rate is an accurate argument because I am not sure how "significant" a drop from $19\mu\text{m}$ to $30\mu\text{m}$ in growth rate is, and a change in growth rate could be from a variety of factors independent of precipitation amount (i.e. chemical kinetic processes, dissolved Ca^{2+} concentration, etc.). I recommend strengthening your argument on this (are their regional proxy records that suggest there was reduced precipitation amount at this time?) or removing the growth rate stance as a whole. Also, the interpretation is also made that "in-cave gas exchange processes are the most likely explanation for the strong $\delta^{13}\text{C}$ variability", and bedrock dissolution/fractionation processes are ruled out. There should be clarification for what you mean by "in-cave" gas exchange processes, because right now you make this interpretation, yet right before you rule out bedrock dissolution and fractionation mechanisms. *Also, why are the distinct isotopic changes at ~ 5 and 6ka not discussed? At both of these times, it appears $\delta^{18}\text{O}$ and dcf ($\sim 6\text{ka}$), and $\delta^{13}\text{C}$ and dcf ($\sim 5\text{ka}$) change drastically. Also at 6ka the dcf increases greatly – what could cause this? Why is this not mentioned? It definitely should be if the steady increase in dcf in the younger part of the sample is discussed (I find the sharp changes at 6-5 ka to be more significant than the younger part of the sample).

3. 2.4-3.8 ka: The more stable $\delta^{13}\text{C}$ signature and increase in dcf suggests a contri-

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bution of aging OM reservoir. This old OM reservoir source is suggested to have been from the buildup of a mid- Holocene warm epoch. Overall, I follow this interpretation and thinks it makes sense. How/why is there the rapid decay trend of F14C at $\sim 6\text{ka}$?

Comments: Overall, I think this is a nice study and will make a worthwhile contribution to the literature. I think a future of combining novel high-resolution ^{14}C measurements with other stable isotope data will definitely aid in the interpretation of these systems in terms of climactic processes. I think a bit of reworking with the discussion to help overall flow and clarifying several sections will result in a nice manuscript.

Some care should be taken when lumping speleothem “growth rate” with these interpretations – however, as a reduction in growth rate is not always a direct relation to reduced precipitation [i.e. changes in chemical kinetics, flow conditions (turbulent vs. laminar) could also control the growth rate of speleothems]. More of this is noted below, but this was one main issue I had with the interpretations.

I think this paper would strengthen if there was a brief, added section on what the initial ^{14}C (F14C) raw values can tell us, vs. what the dcf tells us. The paper mentions what factors can contribute to dcf (lines 78-92), but it would be good to mention what the initial ^{14}C values can tell us in this section as well. Especially because the F14C is referred to at the end of the paper (during the discussion of the youngest part of the sample, and in Fig. 6), which becomes slightly confusing because the entire paper is centered around the dcf values. I understand the distinction between the two (the use of initial ^{14}C values to calculate for dcf) but adding a sentence to explain why you would look at raw, initial F14C values vs. dcf would be beneficial for overall flow and clarity of the manuscript and interpretations.

In addition, there are lots of data in this manuscript and I’m confused what all your study specifically measured (the radiocarbon) vs. what data from other studies you are comparing it with (i.e. $\delta^{18}\text{O}$, $\delta^{13}\text{C}$? Did you all measure $\delta^{13}\text{C}$?). I would make this clearer in the methods somewhere by stating directly: “in this study, we measured

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radiocarbon and compared with XYZ from other studies.”

Comments on tables & figures: Table 1 – Why is there a “*” after the “expected” in the table. I see no explanation of this. Also, under the “Expected* 13C” column of the “Old OM contribution to seepage water acidification” row, does the “shift to more negative values” mean <0 or <10? If it’s closer to <10, I’d label it like that since that’s what you have in the above two rows (for consistency).

Figure 1: There is no ruler in this photo. It says the length in the caption, but it would be helpful to have a ruler for reference. This would especially be helpful when looking back at this figure during the discussion when you say the “old section of SPA 127 (>8,ka, >120mm)”, because then we’ll be able to go and see where in the sample this is.

Figure 2: Are the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ from other studies? If so, cite the studies in the figure caption after part (C).

Figure 2: Also, it would be helpful to plot the age in this figure (since age is what you refer to in the discussion, not depth). You could add it by an additional x-axis on the top.

Figure 3: You mention that “12CHE” is the signal intensity in the figure caption, but nowhere in the text do you explain this further. Can you add a section somewhere that says this? It becomes confusing during the discussion section (e.g. lines 270-273), because in these sections you refer to it only as “12C”, and not 12CHE”.

Figure 4: What stands out to me is the jump at 6ka (increase in dcf, decrease in $\delta^{18}\text{O}$, and decrease in $\delta^{13}\text{C}$), but this isn’t mentioned in the text at all? How come?

Figure 4, overall comment: “the yellow, white, and orange shaded areas represent phases with distinct stable isotope and dcf characteristics. . .” but what about the two sections (1: ~6ka when dcf increases and dO^{18} and $\delta^{13}\text{C}$ decreases; 2: ~5ka when $\delta^{13}\text{C}$ and dcf drops)? These transitions aren’t really talked about in the text, and I’m

wondering why you chose not to select these areas as “phases” with distinct characteristics?

Figure 4c: How do you know there are not hiatuses in between the U-Th ages? For example, it appears right before an age of 4 (the yellow/white boundary in panels 4a and 4b), there is a sharp decrease in dcf, increase in $\delta^{18}\text{O}$, and increase in $\delta^{13}\text{C}$, yet this is the part of your sample that has the longest gap of age control. How do you know there’s not a micro-hiatus here that’s undetectable? It may be worth mentioning you can’t rule this hypothesis out, just to cover your bases and to let readers know you thought of this (rather than just interpreting this as a purely real signal). Also, the U-Th ages need error plotted.

Comments by line: Line 60: Can you give a few examples in this sentence of what you mean by “in-cave processes”? I see you cite Matthey et al., 2016 and Spötl et al., 2005, but it would be easier for readers to follow what you mean by this by stating it clearly in the sentence.

Line 83-85: You mention the conditions in both an “open vs. closed” system can affect the dcf, but you only describe how the dcf typically is in an open system. I suggest adding a sentence describing what dcf would be in a closed system for clarity. Also detailing how there could be a change from an open to closed system may be helpful. I see you outline it in Figure 5, and also in Table 1, so perhaps just simply referencing these two figures/tables will help streamline this discussion.

Line 88-92: “Several studies...more closed-system conditions under higher precipitation regimes”...maybe reword this sentence because I’m not sure what exactly you mean by it. What constitutes “more closed-system” conditions? Once again, perhaps by referencing either Table 1 or Figure 5 this would help.

Line 136: How do you know there aren’t hiatuses present in your speleothem? Perhaps briefly state how you approached assessing hiatuses in your sample here. Also what is the error on each age? I don’t see this stated anywhere, and it’s not in Figure 4C.

The error should be plotted.

Line 162-163: “offset between stable isotope and radiocarbon data of up to several hundred micrometers”, how did you go about accounting for this? Perhaps briefly describe what you did to account for this offset so readers are aware of your methodology. *I see in line 350 that you are unable to apply a correction factor. Perhaps stating this earlier (such as at line 162-163) will help the reader better understand your process of approaching this.

Line 193: It should be stated in the first sentence or two what you used this technique for. Example, directly stating: “FTIR was used for. . .”, because right now it is unclear why you used FTIR (it’s not until later in the discussion when you explain identifying the contaminated epoxy area, and I think it’d be better to state up front in this section). *Line 276: “it’s exact composition has been determined using FTIR”. It is not until this sentence that I realize what you are using FTIR for. Perhaps add a sentence to the FTIR section (the section starting at line 193) that states, “we use FTIR to determine specific compositions of areas in our sample to clarify the causes of anomalies.”

Line 243: “For the more than 1500 radiocarbon data points”, I suggest just inserting the exact number of data analysis points that you have here, instead of saying “more than..”

Line 259: Please add a reference at the end of this sentence to let readers know where the “previously published $\delta^{18}\text{O}$ values” can be found. Also, did you measure the $\delta^{13}\text{C}$ values in this study? Or did you pull data from another study? This is unclear and should be clarified.

Line 265: I think this paragraph could be reworded so it’s clearer. I’m a bit confused about how the different sections of the discussion are broken up the way they are. A suggestion: section “1. LA-AMS anomalies in the old section of . . .” should be an entirely separate section than the ones below, because it just details how the presence of epoxy caused contamination, and there are no other interpretations of the data as-

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sociated with it. This entire section be a brief paragraph at the start of the discussion section, and then you could transition into a “part II” of the discussion that’s exclusively about the interpretation of the isotope systems across different parts of the sample.

Line 266: A suggestion to clarify this sentence: “..in the bottom part of the sample”

Line 270: Please add the reference to Figure 3 after this sentence: “The five ^{12}C -cururent peaks correlating with... (Figure 3)” so the readers know this is what you’re referencing. Also change “indicating” to “indicate”.

Lines 300, 328, 335, 337, 339, 396, 397: Change “C” to “C-isotope”. I probably missed additional places you refer to just “C”, so please change everywhere this occurs.

Comment on section “2. Old section of SPA (>8 ka BP) (Line 293-315): The first paragraph of this section (line 294-309) walks readers through interpretations of high dcf values and low $\delta^{13}\text{C}$ values from >8ka. A transitional sentence is needed in the beginning part of the second paragraph (lines 310-315), to set up the connection of the two (i.e. the warmer temperatures for the Holocene could have caused the mobilization of the older OM), because right now it feels out of place a bit. Also adding a concluding sentence would be beneficial to wrap up this section of the discussion.

Line 319: Perhaps state at what depth/age you are referring to here in this sentence. For example: “As indicated by the reduced growth rate in SPA 127 (Fig. 4, 3.8 ka)..”

Line 320: Misspell of “precipitation” (it says “recipitatoin”).

Line 321: Please add this to the sentence for clarity: “The low $\delta^{13}\text{C}$ -values of the first growth period are superseded by rapid and very large variations of $\delta^{13}\text{C}$.”

Line 325-328: You state here “the dcf between 3.8 and 8 ka is generally lower than the older section. . .” but at ~ 5.8 -6ka dcf jumps relatively high and stays high until ~ 5.2 ka. I think this should be addressed somewhere in your discussion.

Line 343, 392: what is (Fig A7?) Do you mean supplemental Figure 7 (Fig S7)?

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Line 330: Hypothesis 1, general comments – Line 351: “a positive correlation between main features of $\delta^{13}\text{C}$ and dcf are observable for the middle period, especially between 3.8-5 ka and 6-8 ka BP.” I would argue @ 4ka they appear reversed, but 6-8ka I believe I see this correlation. A suggestion: zoom in on these two time slices for what’s plotted in Figure 4B, especially the 6-8 ka one, so the correlation is clearer (the blue and orange lines are kind of on top of each other in the figure now so it’s hard to see. . .). The argument for this could be stronger if you could demonstrate the relationship more clearly. Line 354: A bit more explanation for why “an increase of the dcf to 100%” is needed for this mechanism to work would help the flow of this argument better. Line 355: “Generally, the dcf is even smaller than in the youngest and oldest section of the stalagmite..” What about at from 6-5ka? This need addressed.

Line 354: “..this is expected to be accompanied by an increase of the dcf to 100%.” Why? Some elaboration on this would strengthen your argument.

Line 362: Hypothesis 2, general comments – Overall the text in the discussion of this hypothesis is clear. But I disagree with your growth rate argument. As stated in previous comments, I’m not sure if a change in the growth rate ($19\mu\text{m}/11\mu\text{m}$ to $30\mu\text{m}$) is “significant” – I consider this just a “lower” growth rate. I therefore don’t think you can use this piece of information to suggest it was caused by an overall reduction in precipitation amount. I think you should either try to bring in literature that demonstrate regional drier conditions, or some other support for this argument other than growth rate.

Lines 395-427: I’m a bit confused with this paragraph. I follow your discussion, but are you saying this is your main interpretation for what is happening during this interval and causing all the fluctuations? (i.e. is this what you mean by “in-cave” processes). You state in the conclusion that it’s not bedrock dissolution or fractionation processes, so are you interpreting the strong variability in $\delta^{13}\text{C}$ as a change of gas exchange processes? If so, this needs to be stated clearer, because right now it’s a bit ambiguous whether you mean this or not.

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