Response to Reviewer Comment 1 (reviewer comment in black, response in violet and revised text in blue).

The manuscript "Distinguishing vegetation and soil component of d13C variation in speleothem records from degassing prior calcite precipitation effects" by Stoll et al. presents a high quality scientific contribution to the interpretation of speleothem proxy records, in particular carbon isotopes, as well as the trace metal ratios (Mg/Ca) and (Sr/Ca) also explored in the manuscript. It is within scope of Climate of the Past for the development of methods and understanding of speleothem proxy data, as well as some new data in the case studies. The results and interpretation well-argued and presented in an appropriately structured way in terms of text and figures/tables.

The approach is novel and the methods valid. The manuscript is particularly well-presented in its presentation of the complexity of carbon isotopes and PCP, providing a useful review of these proxies as well as a novel method towards improved quantification of proxies. The paper also well-outlines the uncertainties in the approach and then develops a method to numerically incorporate these uncertainties into the quantification of the impact of degassing/PCP on speleothem carbon isotopes. It is shown that while the uncertainties preclude a reconstruct an actual soil CO2 d13C value, it is shown that the method may still be applied to examine the impact on the trend of the reconstructed soil δ13C compared with the measured δ13C values in the speleothem. This is the strength of the paper and is well-illustrated in the case studies. I appreciated the detailed appraisal of the method and output.

As well as providing a method for correcting the PCP impact on d13C via Mg/Ca, my impression of other strengths of this paper are also is in its demonstration that speleothem DMg may vary within a speleothem time series and that this may actually be expected to be common. I think that this point is an important contribution to the community and it is well-explored in the paper, although please see point below about fabrics and flow paths. The other major finding that I think should be useful to the community is that the soil PCO2 and PCP processes can have counteracting influences on the resulting stalagmite δ13C and produce observed nearly constant δ13C timeseries during significant climatic transitions. It is demonstrated in the two case studies and provides good motivation for others to investigate their datasets with this method.

There appears to be cave monitoring paper from the same cave(?) in review (Kost et al) that this was not cited in the reference list. If it were (and if in open access review?), it would have been interesting to see whether these monitoring data support the approach presented here. Hopefully, this is covered in the Kost paper.

The Kost et al. monitoring study, in the review process since 2021, is now published and the full citation will be included in the revised manuscript. It is:

Kost, Oliver, Saul González-Lemos, Laura Rodríguez-Rodríguez, Jakub Sliwinski, Laura Endres, Negar Haghipour, and Heather Stoll. "Relationship of seasonal variations in drip water δ 13 C DIC, δ 18 O and trace elements with surface and physical cave conditions of La Vallina Cave, NW Spain." *Hydrology and Earth System Sciences* v 27 2023 (2022): 1-42. https://doi.org/10.5194/hess-27-2227-2023.

As outlined above, the authors have well-outlined the uncertainties in their approach, although there are two other possible processes that were not or perhaps under-acknowledged. One is the the recent findings by Frisia et al 2022 in Quaternary Science Reviews. This paper showed that Mg/Ca in the calcite may vary with fabric porosity. This will affect the partition coefficient, DMg, which feeds into the equations for correcting PCP impact on d13C. This should be included and the findings of Frisia et al paper also implies that the Stoll et al manuscript would benefit from a description of the fabrics and whether they differ within a stalagmite over sections where DMg is thought to have varied.

We appreciate the reviewer alerting us to this new paper. We propose adding the citation to Frisia et al 2022, which was published after our manuscript submission, in section 5.2.1.

Future field monitoring and farmed calcite studies should also evaluate whether calcite fabrics could provide independent evidence for variation in DMg, since some stalagmites show relationship between fabrics and Sr partitioning (Frisia et al., 2022).

In the background information on the samples, we propose to provide information on fabrics for several stalagmites where such data has been previously published:

The slowly growing fossil stalagmites consist of dense calcite and show no evidence for columnar porous fabrics. Stalagmite calcite for GAR and GAL consist of predominantly columnar compact to columnar open fabrics (Sliwinski and Stoll, 2021). Similar fabrics are confirmed in GUL and GAE(Sliwinski et al., 2023). Samples ROW, BEL, and NYM fall exhibit growth rates (12-40 μm/yr) similar to GAR, GAL, GUL, and GAE and feature similar dense, nonporous macroscopic textures. The much more slowly growing GLO and GLD likewise feature dense, compact calcite comparable to sample GLA with similar growth rate and described as columnar and columnar open (Kost et al., in review).

This includes a citation to the following paper, which presents multi-technique examination of fabrics and trace element maps on active and fossil samples from the same cave setting We will provide updated citation when its review process is complete.

Kost, O., Sliwinski, J., Gies, N., Lueder, M., and Stoll, H. M.: The influence of fluid inclusions, organics, and calcite fabric on trace element distributions in stalagmites, Frontiers in Earth Science, in review.

The potential for speleothem fabrics to provide further clues on changing partitioning coefficients is one which clearly merits further study, because we identify the potential for variation in DMg to be a key uncertainty in quantitative estimation of PCP. Our results comparing δ^{44}Ca and Mg/Ca suggest that the DMg may be systematically increased as dripwater Mg/Ca increases, ie DMg may covary with PCP in a given stalagmite. In the revision in section 5.2.1, we propose to clarify that these relationships should be carefully investigated in future experimental and cave monitoring studies, in which the DMg can be independently calculated. In fossil stalagmites, in which the dripwater composition is not independently constrained, we expect that it could be difficult to ascertain the causes and consequences of correlations among PCP, fabrics, growth rate, and DMg. Also considering the suggestion of Reviewer 2, that the manuscript and its figures are currently too long and should be reduced, we refrain from introducing further complexity in this paper with addition of fabrics, and underscore that this is an important avenue of investigation for future work with the following statement:

Future field monitoring and farmed calcite studies should also evaluate whether calcite fabrics could provide independent evidence for variation in D_{Mg}, since some stalagmites show relationship between fabrics and Sr partitioning (Frisia et al., 2022).

Similarly, karst flow paths received one brief mention around line 310 yet there has been much discussion in the literature around flow paths and PCP. The manuscript should include a few more sentences around this, rather than focus on PCP has just being a function of CO2 gradients and drip rate. Finally, the fabrics and even speleothem morphology can provide a useful indication of past drip rates and this is covered in multiple other studies and in the Speleothem Science book by Fairchild & Baker. Seeing as the influence of drip rate on PCP appears to be important yet we cannot know how drip rate has varied in the past, some description of the fabrics and speleothem morphology could have been helpful as these can be an indication on whether drip rate has varied in the past.

We thank the reviewer for these suggestions and propose to take up karst flow paths in more detailed discussion of PCP. We propose expanding the second paragraph of section 4.4.1 to clarify this issue:

In addition to the oversaturation state, PCP is also dependent on the degassing time. PCP can occur in air-filled voids above the cave as well as on walls and ceilings of the cave prior to the landing of dripwater on the studied stalagmite. Here, we discuss the integrated PCP, regardless of where along the flow path PCP has occurred. The susceptibility of a given speleothem to PCP may depend on the geometry of the flow path. Temporal variations in PCP in a given stalagmite are expected to depend on the flow (e.g. drip rate) as well as on the oversaturation.

Other points:

More correct wording of the title may be: “Distinguishing soil component of d13C variation in speleothem records from degassing prior calcite precipitation effects”. The approach is not able to specifically isolate vegetation d13C from the soil d13C CO2 pool and does not discuss vegetation-derived d13C CO2 at any length in the manuscript.

We thank the reviewer for the suggestion to clarify the title. We proposed to distinguish the joint soil and vegetation processes from the degassing/PCP process, we do not propose that further deconvolution can be made to separate soil effects from the vegetation of the soil and epikarst. For this reason our target variable is described as the $d13C_{init}$, the isotopic value of DIC after soil and vegetation interaction, but prior to degassing and PCP.

We propose that a clearer title may be adding the word combined to clarify that the initial d13C signal is set jointly by the vegetation and soil processes:

Distinguishing the combined vegetation and soil component of δ13C variation in speleothem records from subsequent degassing and prior calcite precipitation effects

We also propose in the introduction, to clarify

This soil and vegetation signature imparted to the dripwater is also imprinted on speleothem $\delta^{13}C$.

L19: the term “overprinting” is used to describe PCP on speleothem $\delta^{13}C$ here and throughout. Suggest “contribution” would be more correct term.

We believe it is helpful to distinguish between the initial signal attained by dripwater equilibration with CO_2 from soil and deeper respiration, a signal we refer to as $\delta^{13}C_{init}$, from the subsequent evolution of this signal due to degassing. We selected overprinting as it conveys the generally sequential process, and suggest to retain this term.

L22: “universally”, this is not a global study so the conclusion can only be that PCP is not the dominant control on this particular study site. Suggest reword.

We thank the reviewer for the suggestion to reword, which we will implement.

L28: this sentence is unclear and needs rewording, suggest: “During glaciations, calculated initial δ13C implies trend of increasing respiration rates and higher soil CO2, despite the interpreted reduced drip flux to favour more extensive PCP”?

We thank the reviewer for the suggestion to reword and clarify, which we will implement as follows:

During deglaciations, calculated initial $\delta^{13}C$ implies a trend of greater respiration rates and higher soil CO_2, although the higher interglacial dripwater saturation favors more extensive PCP.

L32: Why not the lower latitudes? Doesn’t Figure 4a contradict this introductory sentence?

We thank the reviewer for the suggestion to reword and clarify, which we will implement. We agree that changes in vegetation productivity and soil processes significantly influence the $\delta^{13}C_{init}$ across all latitudes. Now, we have added the focus on mid and high latitudes to the fourth sentence instead, where we discuss the climate sensitivity of respiration rates, to emphasize that only in the mid to high latitudes is temperature likely to limit respiration rates. This paragraph then would read:

Changes in vegetation productivity and soil processes significantly influence the $\delta^{13}C$ of dripwater. The $\delta^{13}C$ of CO_2 in the soil and karst reflects the relative contributions of isotopically light respired CO_2 and isotopically heavier atmospheric CO_2. Conditions which favor higher vegetation productivity and faster rates of heterotropic and autotrophic respiration in soils will lead to higher soil pCO_2 and a lower $\delta^{13}C$ of CO_2. In contrast, in less productive and slower respiring systems, the atmospheric CO_2 and its higher $\delta^{13}C$ will be more significant C sources in the soil. This soil and vegetation signature imparted to the dripwater is also imprinted on speleothem $\delta^{13}C$. In the temperature range characterizing the mid- and high latitudes, respiration rates and vegetation density are highly sensitive to temperature, and speleothem $\delta^{13}C$ has been exploited to serve as a temperature proxy in mid-latitude speleothems(Genty et al., 2006; Genty et al., 2003).

L39: root depth and soil moisture content also contribute.

We thank the reviewer for the suggestion to reword and clarify. We have added the reference to Meyer et al 2014 here, which discusses the significance of deep-rooted trees to maintaining a high column-integrated CO2 and open system dissolution. We also note the role of sufficient soil moisture in maintaining high soil CO_2 citing Romero-Muialli et al 2019 .

Table 1: looks like a copy and paste mistake for scenario A1 and A2 as identical definitions given for these variables. This made it a little hard unfortunately to understand some of the distinction in the modelled results for these two scenarios although I don't think was an important factor in being able to follow the main findings of the paper. But needs fixing here. Also, Delta Ca should be Delta44Ca.

We thank the reviewer for suggestions to clarify the table 1 notation. There is NOT a copy and paste mistake regarding scenario A1 and A2 in Table 1. Both scenarios A1 and A2 employ constant ΔCa, but with a different choice of its value. For each stalagmite, the precise value of ΔCa in A1 and A2 is specified in Table 3. We propose to adjust the table to provide a single line for scenario A1 and A2 so that they share the common description. We will also adjust the notation of $\Delta 44Ca$

L167: suggest precipitation rate rather than growth rate dependent, i.e., the loss of calcium is not necessarily related to growth rate. Growth rate is usually used to define the linear extension rate in the vertical axis of a stalagmite.

We retain the term growth rate in the discussion of the fractionation factors, since growth rate is the term employed in the cited DePaolo, 2011 and Mills et al 2021 references.

Sub-heading 2.2.3. Are there a few more papers on D44Ca and PCP worth citing here?

In this section 2.2.3, we cite only studies which have presented both Mg/Ca and d44Ca on paired samples, in order to compare the results from both indicators. We have added a subsequent study on Heshang Cave (Li et al., 2018) to the cited Owen et al study (2016). Other studies reporting d44Ca but not Mg/Ca are cited elsewhere, including De Wet et al 2021 (cited in section 2.2.2 introducing Ca isotopes as PCP indicator).

L216-217: is this statement supported by the back modelling in the results?

We are now able to update the citation here for monitoring results, which provide full support for the statement

Kost, Oliver, Saul González-Lemos, Laura Rodríguez-Rodríguez, Jakub Sliwinski, Laura Endres, Negar Haghipour, and Heather Stoll. "Relationship of seasonal variations in drip water δ 13 C DIC, δ 18 O and trace elements with surface and physical cave conditions of La Vallina Cave, NW Spain." *Hydrology and Earth System Sciences* v 27 2023 (2022): 1-42. https://doi.org/10.5194/hess-27-2227-2023.

L222: please add the mass spectrometer specifications.

We infer the reviewer is suggesting that the detail the analytical reproducibility provided in the Breitenbach and Bernasconi reference. We will add the precision is 0.08 ‰ for both isotopes.

L231: please reword as it is unclear as to whether there were five repeats on each aliquot or whether there were five analyses performed on each stalagmite?

We now clarify that a minimum of 5 analyses were conducted on each aliquot.

L240: preferred value rather than preferred measurement?

We refer to Mg/Ca as the preferred measurement relative to $\delta^{44}Ca$. We have adjusted the sentence for greater clarity.

L253: please refer back to equation 3 here.

We will add the reference to equation 3.

L300: La Vallina Cave?

Thank you for prompting us to clarify that we refer to La Vallina Cave, in Porrua.

L300 paragraph starting here becomes confusing as total range and “fold” range not the same thing. Confusion ensues here for several paragraphs until the reader sees the definition of range used is the maximum/min rather than max minus min value. This definition does not come until the caption in the following table. Please define in the text to assist the reader.

We thank the reviewer for prompting us to clarify the term. We propose to define the range of variation in at the onset of the paragraph.

In the full geochemical sampling of the 8 speleothems from La Vallina Cave, Mg/Ca variation in a given stalagmite ranges between 1.7-fold and 3.5-fold, with the exception of GAE (12.2-fold range).

Fig 4 caption: for soil moisture which direction was the experiment? Do the green crosses indicate increasing or decreasing soil moisture?

We propose to clarify the figure caption by rewording:

In a second case shown with green crosses, variable initial Ca corresponds to constant temperature, simulating decreasing soil pCO_2 limited by decreasing moisture at constant temperature.

L432: there should be some earlier description of these dripwater measurements and their method, seeing as the Kost et al paper is not yet published.

As noted above, we are now able to cite the Kost et al monitoring paper.

Reference:

Silvia Frisia, Andrea Borsato, Adam Hartland, Mohammadali Faraji, Attila Demeny, Russell N. Drysdale, Christopher E. Marjo, Crystallization pathways, fabrics and the capture of climate proxies in speleothems: Examples from the tropics, Quaternary Science Reviews, Volume 297, 2022, https://doi.org/10.1016/j.quascirev.2022.107833.

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Kost, O., Sliwinski, J., Gies, N., Lueder, M., and Stoll, H. M.: The influence of fluid inclusions, organics, and calcite fabric on trace element distributions in stalagmites, Frontiers in Earth Science, in review.
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