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

General comments.

Unraveling paleoclimate signals from speleothem geochemical proxies is an important challenge to address in order to maximize applicability of such proxies. This manuscript combines TE/Ca and calcium isotopes to act as a proxy for degassing and prior calcite precipitation (PCP) and remove the effects of those two processes on stalagmite d13C records. This in turn allows one to interpret stalagmite d13C time series in terms of climate-driven variations in vegetation and soil. The authors use coeval speleothems from a single cave to produce several records to apply their models. A key part of the approach is separating the temporal trends in PCP from those due to soil/epikarst components within a stalagmite. The results show potential for d13Cinitial records to show climate shifts, and that such d13C records are difficult to use without multiple other proxies in the same speleothem. The results for multiple coeval stalagmites indicate that the δ13Cinitial approach may resolve soil/vegetation changes driven by regional climate changes.

The manuscript discusses changes in Mg/Ca and Sr/Ca (TE/Ca) in terms of two principal processes - either PCP or changing partition coefficient. The possibility of water-rock interaction (WRI) is offered as an afterthought, without adequate justification for largely discounting it as a key process to be considered. The impact of WRI on TE/Ca, and therefore on unraveling the extent of PCP, is not well addressed. It's not until page 11, line 305, that WRI is brought up as a possible factor, where it is stated that WRI is not necessary to attain the Mg/Ca range observed for the stalagmites. This misses a key point, however, that WRI – while not necessary – cannot be ruled out as an important process in karst water evolution. In this case, d13C evolution by WRI in the epikarst may occur, and change the interpretation that assumes that all above-cave processes that change water DIC d13C are due to changes in climate/vegetation/soil. There are examples in the literature of how the multiple effects of WRI and PCP can be parsed out in well understood karst systems. Quantitative approaches to this using TE/Ca and Sr isotopes can be found in Wong et al. (2011, GCA) and Sinclair et al. (2012, Chem. Geol.) There are several places where this issue is further explained in the Detailed Comments below.

We thank the reviewer for the suggestion to provide a more systematic and unified discussion of the potential variation in the trace element/Ca (TE/Ca) ratio attained as a result of bedrock dissolution prior to PCP, which was previously described in disparate sections (lines 176-180, 215-217,383-385,585-586). We propose to add a paragraph at the end of the background section 2.2.1 to clarify the role of dissolution/water rock interaction.

The use of Mg/Ca (or Sr/Ca) as a quantitative indicator of PCP also requires that the initial dripwater Mg/Ca attained by karst rock dissolution prior to PCP remain constant for a given dripwater site and stalagmite over the time period of interest. Yet, in karst rocks composed of heterogeneous carbonate mineralogy, there is potential for variation in initial dripwater trace element/Ca ratios. In karst rocks composed of both dolomite and calcite, the slower dissolution kinetics of dolomite may lead to greater relative dolomite contribution with longer water residence times, leading to higher dripwater Mg/Ca and higher dripwater Mg/Sr with longer water residence times (Tremaine and Froelich, 2013; Fairchild and Treble, 2009). In young reef limestone, primary aragonite and high Mg calcite dissolves more rapidly than diagenetic low Mg calcite, potentially contributing to temporal evolution of initial, undegassed dripwater ratios over time due to progressive meteoric diagenesis of primary phases

(Sinclair et al., 2012). Where bedrock is heterogeneous, it can be useful to define the initial (undegassed, without PCP) dripwater chemistry as resulting from the mixture of the multiple bedrock components, e.g. the bedrock mixing fraction (Tremaine and Froelich, 2013). In a synthesis of published dripwater time series, in 30 out of 32 drip locations (from 11 different cave systems), bedrock mixing fractions remained constant to within 3%, and the temporal variations in Mg/Ca were driven by variable extent of PCP(Tremaine and Froelich, 2013). This compilation suggests that in a large majority of investigated settings, for an individual drip, seasonal and interannual variations in water residence time do not significantly affect the initial Mg/Ca attained through karst dissolution. In the cave system from which our example stalagmite records derive, dripwater monitoring similarly suggests stable bedrock mixing fractions at each drip location(Kost et al., 2023).

In monitoring studies, a constant dripwater Mg/Sr ratio over periods of strongly varying drip rate and water residence time, is an indicator of constancy in the proportion of dolomite/calcite dissolution. When partitioning constants of Mg and Sr in speleothems are constant over time, constancy of Mg/Sr ratio of speleothems may be a useful indicator that PCP, rather than differential dissolution, is the main process responsible for Mg/Ca variations(Tremaine and Froelich, 2013). However, variable Mg/Sr in stalagmites may also be caused by strong variations in the partitioning coefficients of Sr, an interpretation supported by the dependence of stalagmite Mg/Sr and inferred DSr on growth rate in many stalagmites (Sliwinski et al., 2023). In such cases, variation in stalagmite Mg/Sr ratios does not necessarily indicate variation in the dripwater Mg/Sr ratios or variation in the dolomite/calcite relative contribution. Thus, we suggest that monitoring of dripwater systems may serve as the most meaningful check of the potential stability of the bedrock mixing fraction and initial dripwater trace element/Ca ratios.

We propose to further update the following sections so that they employ homogeneous terminology, (that of Tremaine and Froelich, 2013) to describe bedrock mixing fraction as presented in the new text in 2.2.1. This revision involves former lines 215, 581, 615:

Despite site to site heterogeneity, individual drips monitored over an 18 month period show very limited temporal variation in Mg/Sr ratios despite order of magnitude differences in drip rate, suggesting that in this cave, individual drips sample a relatively stable bedrock dissolution source and maintain a constant bedrock mixing fraction.

In our cave system, dripwater monitoring in La Vallina system shows very constant dripwater Mg/Sr ratios seasonally despite order of magnitude changes in dripwater flow rates (Figure 12 in (Kost et al., 2023). This suggests that despite variation in water residence times, there is not widespread or significant variation in bedrock mixing fraction.

Mg/Ca is widely measured PCP-sensitive indicator but can be unreliable in host rocks which feature significant components of widely varying solubility and Mg/Ca which give rise to variation in the initial dripwater Mg/Ca attained by bedrock dissolution before evolution of dripwater by PCP.   Large variations in dripwater Mg/Sr ratios during monitoring may be one sign of varying bedrock mixing fraction.

The writing and referencing need work, including adding sufficient information and citations to support the points being made. The presentation and language can be clearer to explain the many new model terms used. Similarly, the figures can be improved, such as by adding error bars to age determinations and by adding more multivariate analysis for the scenarios presented. I point out some examples of this in the Detailed comments below, but my comments are by no means complete in this regard. The example

suggestions for the writing are aimed at making the scientific message clearer so that readers can get the most out of this study.

We appreciate the suggestion to include error bars to the figures showing age determinations and will implement this, together with the specific suggestions made by the reviewer later in the review.

There are 32 individual graphics within the figures. The impact of the paper does not justify this volume of material for the reader to go through. I think these and the text can be reduced by 25%.

For reducing the number of graphical elements, we propose that Table 2 could effectively move to the supplement rather than the main text. To further simplify the figures, we propose that from Figure 7, panels e, f, and g could be presented in supplement rather than main text. Likewise, from Figure 9, panel b could be presented in the supplement rather than the main text.

In summary, the approach presented is a potential useful step forward for the application of speleothem geochemical proxies. A more thorough exposition of alternative processes, such as water-rock interaction, and improved presentation is needed.

Detailed comments by line #.

Line 20. "the initial δ13C of dripwater". Clarify if this the dripwater once it enters the cave, or once it leaves the soil?

We thank the reviewer for prompting us to clarify this term. We propose to define the initial δ13C of dripwater as the composition prior to degassing and PCP.

1. Are the 8 stalagmites from 8 different caves? From different climate regimes? Different time periods? Why were these 8 chosen?

   In line 210 we had indicated that the reported stalagmites were all from the La Vallina Cave. We will now clarify in the introduction

   We present new analyses of PCP proxies δ^{44}Ca and Mg/Ca on 9 stalagmites from a single cave system which experienced the same climate regime and represent a range of climate states from glacial through interglacial.

23-4. "Fraction of initial Ca remaining at the deposition of the stalagmite layer". How is the initial amount of Ca in fluid determined? Is this the same 'initial' as line 20 'initial d13C of dripwater'? State more clearly.

We propose to clarify as follows: .

 From δ^{44}Ca and Mg/Ca, our calculation of PCP as f_{Ca}, fraction of initial Ca remaining in solution at the time the stalagmite layer is deposited.

24-25. State the magnitude of the uncertainty so the reader knows at the outset how well constrained (or not) this value can be using your method.

We thank the reviewer for this suggestion. We do not propose to provide this information in the abstract, as there is a range of values for different stalagmites which are illustrated in the figures.

1. "spanning THE 94 to 82 ka interval" corrected

" higher interglacial dripwater situation". This phrase does not make sense, rephrase. We thank the author for alerting us to the typo (saturation is the intended word, not situation). The revised sentence will read:

During deglaciations, the trend of greater respiration rates and higher soil CO_2 is captured in the calculated initial $\delta^{13}C$, despite the higher interglacial dripwater saturation favoring more extensive PCP.

2. End abstract with summary of how/where/when other speleothem studies can use this new approach.

We propose to add a sentence at the end of the abstract:

Initial $\delta^{13}C$ can be estimated for active and fossil speleothems from a range of settings, wherever there is confidence that Mg/Ca and/or $\delta^{44}Ca$ provides quantitative indication of past changes in PCP. Further study of Mg partitioning in speleothems will improve the robustness of Mg/Ca as a PCP proxy.

33-35. It will be easier for reader to unravel this building block information for the rest of the paper if this is broken up into two sentences.

We proposed the following revision of these sentences:

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.

40-44. This section summarizes the foundational work of Mickler et al. 2004 GCA, 2006 GSA Bulletin, and as such should cite these.

We thank the reviewer for prompting us to include these early field studies in the introduction, not only the most recent field study of Mickler (2019) cited in lines 86, 643, and 649. The revised sentence now reads:

This process has been demonstrated in lab experiments(Polag et al., 2010; Hansen et al., 2019) and in "farmed calcite" in cave environments(Mickler et al., 2004; Mickler et al., 2006) and can be modeled as a Rayleigh process.

1. Should read 'Superimposed on soil and karst processes are in-cave processes...". We infer that the reviewer is opposed to the initial comma separated clause and propose the following revision:

Superimposed on soil and karst process are in-cave processes which subsequently modify the $\delta^{13}C$ of DIC and thereby speleothem $\delta^{13}C$, as coupled degassing and precipitation of CaCO$_3$ progressively enriches the $\delta^{13}C$ of the remaining dissolved inorganic carbon.

51-3. Sr/Ca dismissed by omission here without explanation.

The rationale for focusing on Mg/Ca rather than Sr/Ca appears later in the paper and we propose to leave the introduction stating only the final employed proxies which are Mg/Ca and $\delta^{44}Ca$.

1. Eq. 1 should be checked for balance, parens, subscripts, etc. We will now write the full equation
2. Move Sade et al., 2022 citation to end of previous sentence. done
3. 'preserve', not 'conserve'. Adjusted as suggested

76-8. Be explicit in the description here. Given the quantitative, sequential, and process nature of your model – it would be clearer to explain that the Ca allows estimate of the extent of calcite precipitation, which in turn allows estimate of the degree of degassing.

Previous modeling has focused on the evolution of $\delta^{13}C$ bicarbonate as a function of the remaining DIC. In contrast, here we focus on the evolution of $\delta^{13}C$ bicarbonate as a function of the Ca remaining in the solution. The Ca remaining in solution allows us to estimate the extent of calcite precipitation, and from this we estimate the degree of degassing (and carbonate precipitation) the solution has undergone prior to deposition of the speleothem. We target Ca as the indicator because trace element ratios and Ca isotopic systems may preserve proxy information about the Ca remaining in solution.

83-6. More than refer to A, define it explicitly. What is a "degassing slope"? Explain here and in Table 1 definition of 'A'.

The term A describes the rate of evolution of $\delta^{13}C$ with progressive degassing and CaCO$_3$ precipitation. We subsequently refer to term A as the degassing slope. A range of values have been proposed for A, from equilibrium precipitation and degassing in CaveCalc, to greater, kinetically-enhanced fractionation during degassing suggested by some laboratory(Hansen et al., 2019) and field (Mickler et al., 2019) studies (Figure 1b; Supplemental Figure 1). The support for each of these values and implications are discussed at length in section 5.3. We complete sensitivity test with a range of values for the parameter A.

Figure 1b. The y axis label does not indicate what phase the d13C is calculated for. We have added this to the figure axis label (it was formerly indicated only in the figure caption)

1. 'landing' better than 'impingement', which is not the proper term here. Adjusted as suggested
2. 'partition', instead of 'partitioning', change throughout manuscript. Partition coefficient is adjusted as suggested throughout.

119-20. "Such a dependence would serve to amplify the Mg/Ca due to increasing PCP". This is an important point, but it is stated cryptically. Be clearer. reworded

126-7. "Deviations from expected PCP control may reflect variation in the partitioning coefficients of Sr (or Ba)." Alternatively, such deviations may reflect other processes such as water-rock interaction (Sinclair et al. 2012, Chem. Geol.).

This section has been fully rewritten and reorganized as presented at the onset of this response.

1. need a comma before 'which' adjusted as suggested
2. "DSr increases with increasing calcite Mg/Ca ratio", see study by Mucci and Morse, 1983, GCA 47, 217.

   We have added the following sentence and citation

   A similar increase of DSr with higher Mg/Ca, observed in laboratory growth in a seawater-like matrix, is attributed to the increased accommodation of larger Sr ions in the crystal lattice when the lattice is distorted by incorporation of Mg ions which are smaller than Ca   (Mucci and Morse, 1983).

Throughout manuscript – use convention of notation for partition coefficients with element subscripted

adjusted as suggested

Page 6, first line. See general comments above about controls of mineral-solution reactions (WRI) and host rock compositions as controls on TE/Ca values in drip waters as an important alternative mechanism. "MgCa" should read "Mg/Ca".

As detailed above, we have added a section on the dissolution process.

1. "fractionation of Ca", do you mean fractionation of Ca isotopes?, yes, we have clarified this

154-7. How is this known? Refer to a reference. Add definition of fract factor to Table 1 and refer to that here.

We have added the citation:

Hofmann, Amy E., Ian C. Bourg, and Donald J. DePaolo. "Ion desolvation as a mechanism for kinetic isotope fractionation in aqueous systems." *Proceedings of the National Academy of Sciences* 109, no. 46 (2012): 18689-18694.

1. "must be assumed…". Or, estimated from farmed calcite and dripwater from other sites in the same cave.

   We adjust to:

   …and must be assumed or based on information from farmed calcite in the same or similar cave settings.

174-8. To make the case for growth rate control, give the growth rates for the stalagmites from the different settings. Alternatively, if growth rate is not important, then do not provide this info for any of the stalagmites.

We remove the information on the growth rate for the Heshang stalagmite.

1. "good quantitative agreement in estimated fCa_δCa and fCa_MgCa". What estimates is this based on?

We adjust the sentence to clarify:

These two studies report good quantitative agreement in estimated fCa_δCa and fCa_MgCa

2. "temperature and dripwater initial oversaturation may not have experienced significant variations". What is this based on? We now clarify:

Relative to glacial-interglacial transitions, the Holocene and last interglacial experienced more stable temperatures, and potentially also more stable dripwater initial oversaturation, both factors potentially contributing to constant calcite-water Δ44Ca fractionation factors.

178-80. How do you rule out variations in water/rock contact times?

We propose to expand this sentence to discuss more fully:

Heshang Cave contains dolomite host rock, and varying water residence times could potentially alter bedrock mixing fraction, altering the initial Mg/Ca of dripwater prior to degassing. However, if this process were significant, it would lead to deviation in the fCa calculated from Mg/Ca compared to that calculated from δ^{44}Ca. The consistency of fCa estimates from Mg/Ca and δ^{44}Ca suggest that variations in water/rock contact times did not result in appreciable variation in the bedrock mixing fraction and initial Mg/Ca from dissolution.

1. Abstract states '8' stalagmites not 9. Corrected.
2. Kost et al reference not in reference list, no date given.(see below)

215-217. This is an important point, so show the data or refer to the figure of the time series that support this statement. Without this constancy of bedrock dissolution source, the model does not work, correct?.... because it is only accounting for PCP and initial soil variability and not WRI and not host rock TE/Ca variability?

As the Kost et al reference is now published, we are able to refer to the figure which indicates the constancy of the bedrock dissolution source, Figure 12, and provide the full citation:

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.

1. Show the age model constraints on the figures as error bars. Indicate such analytical uncertainty on figures or in caption for all figures displaying analytical results. We will modify figures and captions accordingly.

240-4. This is a run-on sentence and difficult to follow. We adjust to:

Mg/Ca measurement is much faster than δ^{44}Ca, and therefore it is common to have Mg/Ca measured for every δ^{13}C$_{init}$ measured in the stalagmite We therefore carry out examples employing Mg/Ca as the preferred measurement for deriving a continuous record of δ^{13}C$_{init}$.

1. may also 'be' calculated: we thank the reviewer for noticing this typo, which we fix

295, and Figure 3. All but one of these data sets are comprised of only two samples, so it is of limited value to consider correlations here. Is there an overall correlation among sites, which would provide a larger data set?

Because the different drip locations may feature different bedrock mixing fractions, and also different Ca isotope fractionation factors, we cannot pool all of the data in a single figure.

1. "The 1.7 to 3.5 fold range could be fully explained by PCP".

    - Alternatively, could these values be explained by water-rock interaction? This should be addressed in the text.

    We have incorporated a substantial background on this issue in 2.2.1 and further address this in the discussion section (end of section 5.2.1, "Quantitative PCP indicators in this sample set".)

    - Is it the range of absolute values that is 1.7 – 3.5? What are the units? This is different than stating 1.7 – 3.5 fold range. There are other places in the text where units can be added for clarity. We have rewritten this section for clarity:

    In the full geochemical sampling of the 8 speleothems from Porrua 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) Five of the 8 stalagmites have Mg/Ca variations of 2-fold to 3-fold (Table 2). The 1.7 to 3.5 fold range could be fully explained by PCP even with no change in DMg, since a 3.5 fold range requires the initial dripwater Ca concentration to be greater than 3.5 times the saturation Ca concentration for the cave conditions. Changes in the Mg/Ca of the initial dripwater, prior to degassing, from varying bedrock mixing fraction, or enhanced Mg/Ca ratio due to increased fluid inclusion density, are not required to attain the range of Mg/Ca in 7 of the 8 of the stalagmites.

2. 'process' should be plural.

305-6. Indeed, WR interaction is not required, but it also cannot be eliminated, and as such this process is not accounted for by the model, meaning that modeled d13C soil values may also have a component of WRI not accounted for, which would lead to inaccurate interpretations of speleothem d13C as a proxy.

The presented approach of estimating δ^{13}C$_{init}$ using a constraint on PCP is valid. As we discuss in several sections, the potential to apply this approach to a given stalagmite depends on the robustness of the quantitative PCP indicators for the particular sample. We have recommended several criteria to assess when Mg/Ca is likely to be more robust and when it is likely to be less robust, including monitoring approaches and screening for factors such as detrital contribution to measured Mg/Ca (in section 2.2.1).

At the start of section 3.4, we discuss the advantages of δ^{44}Ca vs Mg/Ca for the quantitative estimation of PCP, including that δ^{44}Ca is much less sensitive to the bedrock mixing fraction than Mg/Ca. We also present cases where paired measurements show full agreement among the two indicators.

In section 5.2 we carefully review the coherency of Mg/Ca and δ^{44}Ca as PCP indicators, and in 5.2.2 we clearly describe the challenges and suggested approaches of using Mg/Ca for quantitative PCP estimation. Overall, we believe the manuscript presents a balanced overview of the current progress as well as uncertainties and important future lines of research to advance this approach and our accurate interpretation of δ^{13}C time series.

320, Table 2. How are the Age min and max calculated? Why are these given for Mg/Ca and not Sr/Ca?

We clarify that the table reports the age of maximum Mg/Ca and ages of minimum Mg/Ca ratios, as discussed in section 4.1. We have not added the detail for Sr/Ca to keep the table streamlined and concise, because Sr/Ca results are not employed for continuous PCP estimation.

1. (e.g., warm climates… e.g. added
2. Fig. 3b or Fig. 4b? Figure citation to 4b is correct

429-31. Difficult sentence to follow. Also, list ranges of values from low to high.

Because the figure employs an inverted δ^{13}C axis, we retain the current ordering of δ^{13}C values in the text.

1. "is not well in measuredδ13C GAE". Do you mean 'is not well expressed in d13C GAE'? we have added the missing word, expressed.

Fig. 8e. There is a caption but no figure. The extraneous caption has been removed.

1. "Because the extent of degassing and PCP can be strongly conditioned by the drip rate".. and drip chemistry adjusted as proposed

566-8. Alternatively, this could reflect water-rock interaction – see Sinclair et al. 2012.

Elsewhere in the text, we have provided the evidence for limited variation in the bedrock mixing fraction from dripwater monitoring in this cave. We now add a further citation for the partitioning effects to the sentence:

Sr/Mg ratio does not conclusively require variation in non-bedrock sources in either element but could reflect partitioning effects which for Sr are decoupled from PCP, as suggested by strong growth rate dependence of Sr partitioning in stalagmites from this cave(Sliwinski et al., 2023).

585-6. write more explicitly. This is cryptic. We now write:

In our cave system, dripwater monitoring in La Vallina system shows very constant dripwater Mg/Sr ratios seasonally despite order of magnitude changes in dripwater flow rates (Figure 12 in (Kost et al., 2023). This suggests that despite variation in water residence times, there is not widespread or significant variation in bedrock mixing fraction.

1. Mg/Ca is "a" widely…corrected

593-4. How about using monitoring of modern dripwaters instead to use Mg/Ca for quantification of PCP? We have added the sentence

589-90. "'feature significant components of wide varying solubility and Mg/Ca which give rise to strong incongruency of dissolution." This phrase after the 'and' doesn't follow. Mg/Ca of what? this is not equivalent to the first term before the 'and'. It is now revised as:

Mg/Ca is a widely measured PCP-sensitive indicator. However, it can be unreliable in host rocks which feature significant components of widely varying solubility and Mg/Ca if the bedrock mixing fraction varies over time. This can produce variation in the initial dripwater Mg/Ca attained by bedrock dissolution before evolution of dripwater by PCP. Large temporal variations in dripwater Mg/Sr ratios at a single drip during monitoring may be one sign of varying bedrock mixing fraction.

637-642. Why three paragraphs, two of which are just one sentence long? It's all the same topic. We have combined the paragraphs, as suggested.

698-699. The role of ecosystem type in the suggested approach is glossed over.

This refers to the match of interglacial values to those reported for respired endmembers in three ecosystems illustrated in Figure 6.

References cited in response

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