

Interactive comment on “Monitoring stable isotopes in caves over altitudinal gradients: fractionation behaviour and inferences for speleothem sensitivity to climate change” by V. E. Johnston et al.

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Received and published: 6 November 2012

We thank Darrel Tremaine for carefully reviewing our manuscript and taking the time to evaluate the stable isotope fractionation with an expert knowledge of cave processes. Your input will significantly improve the revised manuscript.

General Comments

#1) In general, the discussion of the isotopic fractionation process from rain to soil to cave is not well developed, and some of the statements made are not in agreement

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with the bulk of current literature. It should also be addressed that what the authors are referring to as ‘fractionation’ is actually the difference between expected equilibrium values (predicted from the Kim and O’Neil, 1997 temperature-dependent fractionation line) and those measured in cave calcite.

Reply) As suggested by Tremaine (and also noted in response to Reviewer Scholz, General Comment #1), we will include a new paragraph in the introduction that explains, in detail, the processes from percolation water and bedrock interactions, through to in-cave degassing and precipitation systematics. This will include relevant references to theoretical and modelling studies. Furthermore, throughout the manuscript, the terminology will be updated, in particular $\Delta^{18}\text{O}_{\text{c-c}}$ will be used to refer to the difference between expected equilibrium values (predicted from the Kim and O’Neil, 1997 temperature-dependent fractionation line) and those measured in cave calcite.

#2) Nowhere in this manuscript is it made clear that calcite supersaturation is the driver of calcite precipitation rate and therefore the most critical parameter for understanding kinetic isotope effects.

Reply) The new paragraph (see comment #1) will include a detailed description of the processes of supersaturation and precipitation and how these effect the stable isotope fractionation. As also noted in response to Reviewer Scholz, we do not have SI information for the specific dripwaters corresponding to the isotopic measurements but since this is just a snapshot study a single SI value would likely not be very representative and informative anyway. Therefore, in the revised manuscript we will include SI range information taken from published data from the same caves (often the same drips), which will be provided in Table 2. Despite the data here being presented as a snapshot, all the caves in this study have been monitored for several years, and we have a reasonable handle on their responses to infiltration, ventilation and general carbonate geochemistry. The inclusion of this SI range data will thus allow the discussion in association with the literature suggested by Tremaine.

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#3) The site descriptions and snapshot sample data presented are adequate to draw broad conclusions about calcite isotope behavior. But the important connections between soil $p\text{CO}_2/\delta^{13}\text{C}$, dripwater $\text{DIC}/\delta^{13}\text{C}$, cave air $p\text{CO}_2$, calcite $\delta^{13}\text{C}$ and ventilation are not addressed in full. This may be due to limited snapshot data. The authors state several times that certain caves are outliers to 'expected' $p\text{CO}_2$ values. It should be clear to the reader how these 'expected' values were estimated.

Reply) The original manuscript focused more on the $\delta^{18}\text{O}$ data as we felt that more could be gained from discussion of this data. But in light of the importance of the $\delta^{13}\text{C}$ data, more will be done in the revised manuscript to investigate this data. The second point raised refers to what is meant by an outlier to an expected point. The expected point was referring to that of the best-fit curve on the graph, based on the data from the other caves in this study. This explanation will be made more clear when referring to outliers in the text.

#4) In section 5.3 the authors describe petrography at length, but show limited relevant examples of calcite precipitates from the current study. Either this section should be tailored to provide clear examples of how altitudinal effects (temp, SI, water availability) are preserved in calcite fabric with respect to the current suite of caves, or it should be condensed down to a brief discussion on the controls of columnar to dendritic fabric transitions.

Reply) Due to a limited amount of material available for analyses relevant to the caves in this study, the evidence to support this interesting discussion is admittedly rather lacking. Since the manuscript has many other avenues of discussion, this interesting line of research will be condensed in this manuscript, in the hope that it can be pursued in greater detail elsewhere in the future.

#5) In section 5.7 the authors consider shifts from warm/wet to cold/dry. Given that other geographical regions might exhibit the opposite behavior (warm/dry, cold/wet) it might be interesting to explore isotopic fluctuations expected during transition between

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those two endmembers.

Reply) In section 5.7, we had chosen two example end-members climate situations to demonstrate a theory that the in-cave fractionation can either boost or detract from the climate signal. We purposefully did not cover every possible climate setting as this would become repetitive to read and due to the very site specific nature of stable isotope interpretation, may not actually provide an accurate explanation of a situation if used out of context without due thought and attention by future researchers. It is also likely that other climate situations will fall into a category similar to one of the two already explored or have a nature that is exceptionally site specific, and discussion of which is beyond the scope of this paper.

Other comments:

p. 3614; line 23: "Application of oxygen isotopes in speleothems has been particularly successful in determining the intensity of the monsoon." - to which monsoon do the authors refer?

-> This sentence will be re-phrased, as there has been particular success with the application in all monsoon regions. References were provided in the original manuscript to provide some diverse examples.

p. 3617; line 18: "Carrying out the majority of the monitoring during a single month means that the data represent a snapshot in time, and eliminates much of the temporal variability, seasonal and inter-annual, often exhibited in cave data. . ." - I'm not sure that 'eliminates' is the most effective word here because it carries the tone that snapshot sampling is a good way to minimize the effects of seasonal or inter-annual variability that would otherwise complicate the interpretation.

-> Thanks to Tremaine for pointing out this language technicality. We agree that "eliminate" is too strong a word to be used in this context, as it implies the removal of seasonal/(inter-)annual variability. Whereas the snapshot method only means that

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these sources of variability cannot be accounted for, leading to some uncertainty, which is discussed later in the manuscript. It will be re-phrased.

p. 3619; line 5: "Figure 3 demonstrates the strong increase in cave air pCO₂ with decreasing altitude for most of the cave sites. Again BG cave is an outlier to the general trend, exhibiting lower pCO₂ values than expected for its given altitude". - Figure 3 shows a cave site (maybe DL) that has 15,000 + ppmv cave air pCO₂, however Table 2 shows that pCO₂ measured site DL is not higher than 6,035 ppmv. This brings up several issues: 1. Is the lowest altitude cave really 15,000 ppmv? I am not sure that modern calcite would precipitate quickly enough to measure during this study in a cave with 15,000 ppmv. 2. How were the expected values determined? Do the authors mean to say that site BG plots lower than the best-fit line through all data, or is there another way to estimate what the CO₂ should be? 3. If site DL is around 6,000 then Fig. 3 should have almost a straight line through the data points, not a power-fit.

-> We thank Tremaine for finding this notable inconsistency in our results. It has come about because we plotted Figure 3 (cave air pCO₂) using the stable pCO₂ level measured in the deepest part of the caves to understand general pCO₂ distribution with altitude. Whereas Table 2 shows the pCO₂ value taken at the actual sampling sites of active dripwaters and precipitating calcite, which in the case of DL cave occur along the passageway near to the entrance (DL1) and in a chamber approximately halfway along the length of the cave (DL2-4), causing the discrepancy. Tremaine has quite rightly found the reason for a lack of modern calcite formation towards the back of DL cave where ventilation is blocked by a sand constriction and pCO₂ values rise to high levels. To avoid confusion in the revised manuscript, the pCO₂ value will be used from the chamber where most of the measurements were carried out (i.e. 6035 ppm), as the high value is also partly an artefact of reduced ventilation. However, use of this value does not change the power-fit, which remains valid with a good fit (R² = 0.91). With regard to BG, we evaluated that its pCO₂ was lower than the trend ("expected value") based on its plotting below the best-fit line. In addition, in the case of BG cave there

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was an obvious mechanism, namely strong ventilation, that would cause this to be a notable outlier.

p. 3622; line 6: "Both MO and FS caves also exhibit slightly lower pCO₂ than expected for their altitudes". -Please see above comment regarding the expected pCO₂.

-> This was based on their position plotting below the best fit line. However, as a passing comment, this may be deleted to avoid undue confusion.

p. 3623; line 23: "It is therefore reasonable to infer that columnar fabric in speleothems, such as SP1, reflects quasi-equilibrium deposition, although modification of the original dissolved inorganic carbon (DIC) δ¹³C, by degassing at the stalactite tip, cannot be excluded." - The authors have already stated that when compared to the Kim and O'Neil (1997) temperature dependent fractionation line, none of the calcites measured in this study are in isotopic equilibrium. I would suggest that the underlined passage be modified to reflect something like "quasi-constant deposition with respect to the difference between predicted and measured water-calcite fractionation". - From the bold portion of this passage I infer that the temperature dependent water calcite oxygen isotope fractionation is quasi-constant (unaffected by degassing), while degassing may still affect the water-calcite carbon isotope fractionation. It is not sufficient to brush over this important point when considering the relationship between degassing and kinetic fractionation.

-> This will be modified as suggested.

p. 3624; line 1: "Columnar fabric has been found in other high altitude situations. . . as occurring during entrance sealing during glacial advance (Luetscher et al., 2011). - Could the authors provide one sentence here about the source of CO₂ (H₂CO₃) that drives bedrock dissolution underneath a glacier?

-> Given that the petrography section will be shortened in general, this example may well be deleted from the manuscript, as the different situation presented from Milchbach

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Cave does not significantly aid the explanation of our results.

p. 3625; line 3: "With elevated temperatures, and also slower drip rates, the same experiments also found that the $\delta^{18}\text{O}$ calcite deviates further from values expected, given the parent water isotopic composition and cave temperature, than under cooler and faster dripping conditions (Day and Henderson, 2011)". - This increased deviation from predicted values at higher temperatures has been attributed to an incorrect slope of the Kim & O'Neil (1997). Several recent studies have found a lower slope including Tremaine et al. (2011) (16.1), Day and Henderson (2011) (14.92), Dennis and Schrag (2010) (16.02). Most recently Gabitov et al. (2012) found similar results by carefully analyzing lab-precipitated calcite in two different zones: at the center of individual crystals (fast growing; kinetic fractionation), and at the edges of individual crystals (slow growing; close to equilibrium precipitation).

-> Based on the results of these recent studies, this statement will be retracted from the revised manuscript. Its significance on the overall conclusions are minimal.

p. 3625; line 16: "The fractionation amount has then been computed as the difference between the expected $\delta^{18}\text{O}$ calcite and the $\delta^{18}\text{O}$ calcite measured on the cave precipitates". - The difference between predicted $\delta^{18}\text{O}$ and measured $\delta^{18}\text{O}$ is not fractionation. I suggest the authors use notation similar to what has been presented in the literature to express this difference (e.g., $\Delta\delta^{18}\text{O}$ calcite, or more specifically in 1000 $\ln \alpha$ notation). This should be modified here and throughout the manuscript, including lines Figures 7 and 8.

-> What we were referring to, and wrongly naming fractionation amount, has been calculated previously in the literature by Feng et al. (2012) as $\Delta^{18}\text{O}_{\text{cc-e}}$. We will adopt their terminology, along with further use of the more commonly used 1000 $\ln\alpha$ notation, as appropriate in the revised manuscript and figures. However, we note here (and also in the revised manuscript) a caveat of using this $\Delta^{18}\text{O}_{\text{cc-e}}$ terminology because the Kim and O'Neil (1997) equation was only valid between certain temperatures, and a

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number of our cave sites (and those evaluated from the literature), particularly at cold temperatures, are beyond the range valid under the Kim and O'Neil equation (10-40 °C). Therefore, what is being used as the expected (calculated) value is an extrapolation, which may have increased uncertainties.

p. 3625; line 20; "This indicates that with respect to the laboratory experiments, the cave precipitates were always enriched in oxygen -18, which likely occurred through the process of non-equilibrium isotopic fractionation during degassing and calcite precipitation (Day and Henderson, 2011; Mickler et al., 2004, 2006). - Day and Henderson (2011) agreed with the Coplen (2007) assessment that rapid growth-rate driven kinetic effects in laboratory calcite should drive the fractionation factor down, not up (their conclusion #4). In other words, they argued not that cave calcite is too high, but that the Kim and O'Neil (1997) line is too low because of kinetic isotope effects.

-> The reference for Day and Henderson (2011) will be removed from this section, as correctly pointed out, they clearly share the view of Coplen (2007) that the Kim and O'Neil line is too low due to kinetic isotope effects.

p. 3626; line 5: "It likely signifies that within the vadose cave environment it is rarely, or perhaps impossible to reach the conditions of equilibrium found in the laboratory setting (Kim and O'Neil, 1997)". - A recent study at Natural Bridge Caverns by Feng et al. (2012) found several modern calcite precipitates in agreement with the conditions of the Kim and O'Neil (1997) experiments.

-> We have re-analysed the results of Feng et al. (2012) and their manuscript states that in a number of cases the actual dripwater $\delta^{18}\text{O}_{\text{w}}$ was not measured but taken as -4.4‰ an average of measured points (spatially and temporally). The sensitivity to this value is particularly strong, and it was shown that when those values that contained the estimated (averaged, not measured) data were removed from the dataset the Feng et al. (2012) data did not give exceptional values against a large dataset compiled from the literature. We therefore reject the statement implied here by Tremaine that at

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Natural Bridge Caverns (Feng et al., 2012) the modern calcite precipitates are in any better agreement with the Kim and O'Neil (1997) experiments than found elsewhere in the literature. However, we will provide a more detailed discussion of the literature values, including those of Feng et al. (2012) in the revised manuscript, and thank Tremaine for bringing these important data to our attention.

p. 3626; line 11: A reasonable explanation for this is that with a faster drip rate there is less time for the drip to sit at the stalactite tip, and also on the stalagmite surface, where it could undergo CO₂ degassing that cause the isotopic disequilibrium. - CO₂ degassing is not the cause of isotopic disequilibrium; rapid calcite growth after supersaturation has been reached is the cause of isotopic disequilibrium (see Dreybrodt and Scholz, 2011). I suggest that the authors here include a sentence or two regarding the findings of Deininger et al. (2012) where rapid dripwater replacement at the stalagmite tip results in the lowest deviation from expected equilibrium.

-> As also discussed in the response to reviewer #1 (Scholz), we are now better informed and will be providing full explanations for the causes of isotopic disequilibrium earlier in the manuscript, with reference to theoretical and modelling studies. We can then draw from references and illustrations from this earlier paragraph later on in the revised manuscript, as needed.

p. 3627; line 11: "Within a single cave site or cave chamber, factors such as temperature and ventilation are essentially constant". - I do not agree with this statement. There are numerous caves that exhibit seasonal and in some cases daily ventilation such as Obir (Spotl et al., 2005); Hollow Ridge (Kowalczk and Froelich, 2010); Natural Bridge (Feng et al., 2012); Bunker (Riechelmann et al., 2011); and Pere Noel (Verheyden et al., 2008). Furthermore, Tremaine et al. (2011) demonstrated ventilation and temperature driven seasonal variations in $\delta^{18}\text{O}_{\text{calcite}}$ of $\pm 1.5\%$ and seasonal variation $\delta^{13}\text{C}_{\text{calcite}}$ of up to $\pm 2.5\%$ under quasi constant drip rate conditions.

-> Yes, this was a poorly worded sentence, and we obviously share Tremaine's view

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of ventilation changes and have monitored such changes ourselves in the caves of Trentino also. The sentence was meant in terms of a snapshot view, that in an instant (a few minutes to hours needed for monitoring) the temperature and ventilation rate remained essentially constant. Here, we would like to stress the word essentially in this sentence because this entire study is very general, since we take eight very different caves and then make assumptions about their characteristics that allow us to link them together to assess fractionation. The broad assumption that temperature and ventilation remain essentially constant for a short amount of time and within the small confines of that cave chamber, allow other factors that are affecting the fractionation to be narrowed down. The sentence will be re-worded to reflect its true meaning.

p. 3628; line 20: "The approach taken in this study... is a very simple test for isotopic fractionation in a cave". - While I agree that this is a simple test and a good approach, it should be noted here that this test may be complicated if long (seasonal) dripwater residence times create an alias in the dripwater isotopic signature.

-> We thank Tremaine for pointing out this caveat of this simple test and it will be due noted in the revised manuscript.

p. 3629; line 24: "This could be termed the weighting effect and should be quantifiable through the Thornthwaite method (Thornthwaite, 1948), accounting for strong evapotranspiration in summer months". - This passage is not entirely clear to me and I am not sure I completely understand this weighting effect. It is also mentioned again in the next paragraph. Could the authors expand on how the weighted oxygen isotope signal might be quantified by calculating the evapotranspiration using the Thornthwaite method? Does it mean that evapotranspiration causes oxygen isotope fractionation in groundwater, or perhaps that a larger/smaller amount of light/heavy groundwater penetrates seasonally downward into the cave?

-> The weighting effect deals with a difference in the $\delta^{18}\text{O}_w$ values seen in the cave, from that of the annual weighted-mean rainfall amount $\delta^{18}\text{O}_w$, based on the different

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proportions of seasonal infiltration that reach the cave that varies with the amount of evapotranspiration (which varies with altitude). This has been dealt with extensively in the modelling studies of Wackerbarth et al. (2012). The explanation will be enhanced in the revised manuscript with appropriate references.

p. 3633; line 13: "Calcite from Bigonda Cave (BG) consistently shows higher $\delta^{13}\text{C}$ values than expected given its altitude (Fig. 9a). This is due to the water feeding the BG drips being sourced from a much higher altitude than the cave entrance, also seen in Figs. 2 and 3 of cave temperature and pCO_2 . The $\delta^{13}\text{C}$ signal is picked up from where the water infiltrates the bedrock, which according to Fig. 9a is around 1000 m a.s.l." - Calcite $\delta^{13}\text{C}$ values in BG are consistent with what I would expect from a strongly ventilated cave with a sizeable soil cover and biogenic carbon source (Fig. 9a). At low altitude, one half of the DIC in drips comes from soil gas (for example -23‰ , while the other half comes from dissolved bedrock (for example $+1\text{‰}$, resulting in DIC of around -11‰ and ventilation driven CO_2 degassing enrichment of $+2$ to $+5\text{‰}$ to around -8‰ in calcite. This result may not directly comparable to high-altitude caves because the proportions of soil-gas CO_2 and dissolved bedrock are probably not the same. If a higher proportion of dissolved bedrock contributed to DIC, then ventilation degassing effects would lead to significantly more enriched calcite than what is possible inside BG cave (Fig. 9b). If the authors attribute this effect to altitude of percolation waters (as a function of temperature), then it may be useful here for the authors to discuss the temperature dependencies in the water-soil gas-bedrock-DIC fractionation system as outlined by Lambert and Aharon (2011).

-> We thank Tremaine for his insight into the $\delta^{13}\text{C}$ values observed in BG cave with regard to ventilation. In the revised manuscript, we aim to investigate $\delta^{13}\text{C}$ in more detail as from these reviews we feel that this part of the manuscript could provide some more interesting discussion that was lacking from the original article.

p. 3634; Section 5.7: Implications for speleothem-based paleoclimate studies - The discussion in this section is focused on climatic shifts from warm/humid to cold/dry

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conditions, and relative influences of each of these regimes on the isotopic shifts in cave calcite are considered. I would like to see some discussion of what would happen under warm/dry to cold/wet conditions. It may be useful to create a simple table here showing the direction and relative magnitude in expected changes in calcite for each scenario.

-> This discussion was meant to illustrate a principle that in-cave fractionation may attenuate or augment a signal, depending on the factors governing the signal and the in-cave processes. Specific locations and cave settings may vary these factors, so emphasis did not want to be placed on this being a definitive guide to what will happen with that type of cave setting, more so just suggestions to stimulate discussion on future stable isotope interpretation. For that reason a simple table was not used.

p. 3634; line 19: "As an example of two end-member environmental situations, we extrapolate our findings to consider caves where the oxygen isotope composition is dominated by rainfall changes through the amount effect. . ." - I suggest the authors note that there is increasing evidence that some of the variability in Chinese speleothem $\delta^{18}\text{O}$ cannot be accounted for by rainfall amount, and are probably due to source effects (see Clemens et al., 2010; Pausata et al., 2011).

-> It will be clarified in the revised manuscript that the Chinese speleothems are likely dominated by source rather than amount effect, and the discussion as to how this effects fractionation will be tailored to incorporate this view.

p. 3635; line 1: "If the cave temperature was high, the fractionation amount may be higher". - Equilibrium fractionation is reduced at higher temperatures. I infer that the authors are referring to 'fractionation amount' as the difference between predicted and measured $\delta^{18}\text{O}_{\text{calcite}}$. If so, this passage should be modified accordingly.

-> This passage, and throughout the manuscript, the terminology will be carefully controlled and we will use terms such as $\Delta^{18}\text{O}_{\text{cc-e}}$ and $1000\ln\alpha$.

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p. 3635; line 16: "This is in contrast to caves where the oxygen isotope records are dominated by temperature. Warm climates tend to cause high $\delta^{18}\text{O}$ values in meteoric precipitation and hence the dripwater (Fig. 8; in comparison with cool climates)." - I'm not sure this is a fair statement. Figure 8 shows rainfall and cave dripwater $\delta^{18}\text{O}$ as a function of elevation, which is controlled by rainout amount. There is no supporting evidence presented that warm atmospheric temperature (or cave air temperature) controls meteoric or dripwater isotopic composition. My understanding is that the only significant temperature control is during fractionation from water to calcite.

-> This is possibly true and we will adjust the statement and discussion accordingly.

We thank Darrel Tremaine for his thorough review with its constructive comments on fractionation and cave processes that draw on your detailed knowledge of the literature. This will certainly lead to a great improvement to the revised manuscript, for which we are indebted.

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