**Climate
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Discussions**

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*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 Denis Scholz for taking the time to review our manuscript and appreciate his expert opinion on stable isotope fractionation processes that will substantially improve the revised manuscript.

General Comments

General comment #1: "The description of the processes occurring inside the cave and on the speleothem surface (degassing of $CO_2$, establishment of supersaturation with

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respect to calcite, calcite precipitation), their effect on carbon and oxygen isotope fractionation and their dependence on parameters such as temperature, supersaturation with respect to calcite, drip rate, etc. is not entirely correct throughout the MS".

Reply: We thank Scholz for exposing this deficiency in our description and throughout the manuscript. This point will be clarified in the text, plus a brief discussion of processes occurring from the soil to the cave and on the speleothem surface, regarding degassing of CO2, establishment of supersaturation with respect to calcite, calcite precipitation, and their effect on carbon and oxygen isotope fractionation, will be added to the introduction section.

General comment #2: "All the above mentioned processes have been described in detail and modelled in recent publications. . . These papers must be discussed and cited."

Reply: The original manuscript cited a number of publications that the authors felt were the most important for describing the patterns observed in the dataset (e.g. Day and Henderson, 2011; Kim and O'Neil, 1997; Mühlinghaus et al., 2009; Tremaine et al., 2011; Wackerbarth et al., 2012). These included a number of experimental and modelling studies. However, we thank Scholz in drawing our attention to the missing references, which will be discussed and cited in the revised manuscript. In particular, within the new section of the introduction discussing the processes (see general comment #1).

General comment #3: "In some parts of the MS, the language is not precise enough, in particular the discussion of stable isotope fractionation. . . This must be corrected throughout the MS."

Reply: The use of language pertaining to the stable isotope fractionation will be corrected for the revised manuscript. We will remove the term "fractionation amount" that was being used to describe the departure from isotopic equilibrium throughout the text and figures and replace it with the correct nomenclature $\Delta^{18}O_{cc\text{-}e}$, as used by Feng

et al. (2012), as the difference between the measured value and that expected based on the equation derived experimentally by Kim and O'Neil (1997).

Specific comments

p. 3614, line 26: Do Boch et al. (2011) really reconstruct temperature?

- This will be modified as part of the re-structuring of the introduction.

p. 3615, line 6 ff.: Here, a more detailed description of the cave-internal processes including the above mentioned references would be good.

- As stated above (general comment #1), we will be including an description of processes in the introduction section of the revised manuscript.

p. 3618, line 1 ff.: Please clarify if the "calcite powders" were all from stalagmites or also from flowstones or other speleothems.

- This is clearly stated in the final column of Table 2 as the calcite powders derived from a mix of types of speleothems (as growing stalagmites were not always available). Perhaps a text link to this part of Table 2 will be added for clarity.

p. 3618, chapter 4.1: Is the saturation index available for the drip water?

- The saturation index is, unfortunately, not available for the specific dripwaters measured in this snapshot study. Saturation depends strongly on seasonal variability, and a singular value, such as that taken during a snapshot would not be representative. However, the caves used for this study have been monitored (at different frequencies) for several years, including the measurements required for the calculation of saturation index (although not necessarily at the same drip points selected for this study which required active calcite precipitates). Therefore, for the revised manuscript, we will include saturation index range data taken from previous publications dealing with longer-term monitoring of the same caves (Borsato et al., 2007; Miorandi et al., 2010; Miorandi et al., 2005). We can use other parameters monitored during this isotopic study (e.g. pH

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and electrical conductivity) to compare with the published datasets to find where our data lie within the substantial seasonal and inter-annual variability in order to assess the validity of our snapshot data. From these data we will then be able to consider the altitudinal vs. saturation index relationship with confidence. However, we note that this important topic of saturation index and altitude is the primary focus of a forthcoming article on a similar, but more extensive set of caves from the Trentino region.

p. 3619, chapter 4.2: It would be interesting to see how the regional $\delta$18O and $\delta$D data compare with the Global Meteoric Water Line.

- The data line up along the Global Meteoric Water Line (GMWL), with an influence of the Mediterranean Water Line. The interesting aspect raised with this point by Scholz, is that the two different valleys display separate altitudinal trends along the GMWL. Since figures 4a and 4b are similar, the GMWL figure may be substituted for Figure 4b, and appropriate description added into the text.

p. 3620, line 23 ff.: It appears to me from Fig. 6 that the sample with the lowest $\delta$13C value has been used even if its $\delta$18O value is higher than that of another sample. Which $\delta$18O value has been used in this case? Please clarify.

- We indicated the samples that we chose in figure 6 (both $\delta$18O and $\delta$13C from a single samlpe) as the least deviated from equilibrium. The $\delta$18O value used was that corresponding to the lowest $\delta$13C value, i.e. the same as that circled in figure 6. Confusion has arisen here because the $\delta$18O value is not always the lowest value sampled in the cave. The red circle was used initial to clarify this point, but it is obviously not enough, and a clearer statement will be added to the figure caption of figure 6.

p. 3622, line 19 ff.: "... with the degree of isotopic fractionation as either very low ..." Do you mean low or close to the value expected for equilibrium?

- Close to the expected value, this will be updated as part of General Comment #1.

p. 3622, line 27 ff.: "The saturation state being controlled by the reduction of soil

pCO2 with increasing elevation" For the saturation state, the difference between soil and cave pCO2 is crucial. As cave pCO2 also decreases with altitude (Fig. 3), the saturation state does not necessarily have to decrease with altitude.

- Our statement was based on our previous knowledge of the saturation state in the caves with altitude (Borsato et al., 2007; Miorandi et al., 2010; Miorandi et al., 2005), which is predominantly controlled by the altitudinal effect on soil pCO2. However, we acknowledge the importance of the difference between soil and cave pCO2, which will be reflected in the revised manuscript.

p. 3623, line 23 ff.: "It is therefore reasonable to infer that columnar fabric in speleothems, such as SP1, reflects quasi-equilibrium deposition ..." Do you mean close to chemical and isotopic equilibrium here or just not very variable? Please clarify.

- The columnar fabric in SP1 reflects a hydrological, chemical and isotopic system that is not very variable, permitting the columnar fabric to form. It is also likely going to be close to equilibrium deposition, but this cannot be proved with fabric alone. This point will be clarified in the reduced petrography section.

p. 3623, line 24 ff.: "... although modification of the original dissolved inorganic carbon (DIC) 13C, by degassing at the stalactite tip, cannot be excluded." However, as explained above, this effect is not visible in the precipitated speleothem calcite.

- This will be rectified as part of general comment #1.

Chapter 5.3: The discussion of the petrography is interesting. However, as these data seem not to be available for all caves,...... this section may be shortened.

- For cave conservation reasons, speleothems have not been removed from all the cave studied. We will shorten this section relative to the data currently available.

p. 3625, line 6 ff.: It would be good to mention other laboratory experiments (Polag et al., 2010; Wiedner et al., 2008), which have been performed in the framework of DAPHNE, as well.

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- The introduction will cover a wider review of previous work, including laboratory experiments carried out within the DAPHNE framework. From there, examples will be taken for use in the discussion.

p. 3626, line 7 ff.: "This, therefore, infers that all subaerial speleothems are, to some extent, out of isotopic equilibrium." Considering the small amount of data, this statement seems too strong to me.

- Following the concern raised by the reviewer, we have increased the amount of data by taking published isotopic values for active cave calcite, their corresponding dripwaters and the cave temperatures allowing us to perform the same analyses on a larger set of data covering a much wider set of cave conditions. Although, on the most part, the larger dataset show a similar pattern to our original Trentino data, the new compilation highlights that the reviewers concerns were valid and the statement was in fact too strong. Our new compilation indicates that in comparison with estimates of $\delta 18Oc$ calculated using the Kim and O'Neil equation, most cave calcites exhibit higher $\delta 18O$ values than those estimated, resulting in positive $\Delta 18Occ\text{-}e$ values, the magnitude of which indicates their deviation from equilibrium. Our new results indicate that less than 5% of the data exhibit a $\Delta 18Occ\text{-}e$ below 0.25 ‰ which would indicate that only these could be deemed to be within an acceptable level of equilibrium within the bounds of our current understanding and the assumption of Kim and O'Neil equation being correct.

p. 3626, line 11 ff.: The deviation from the equilibrium value does not result from degassing or kinetic fractionation but only from the ongoing Rayleigh distillation during precipitation.

- We will adjust the revised manuscript to reflect this updated opinion.

p. 3626, line 14 ff.: In this context, it may be worth to discuss the recent modelling results of Deininger et al. (2012), who describe the effect of evaporation and ventilation of speleothem stable isotope fractionation.

- Discussion of recent modelling results will be added into the revised manuscript.

p. 3626, line 19: What is meant by "DIC-depletion"? Please clarify.

- All terminology will be updated according to recent publications, as specified by the reviewer in the general comments #1-3.

p. 3626, line 23 ff.: "...there is a trend towards [less deviation from equilibrium of] 18Ocalcite with higher altitude, and thus lower temperatures." …. Anyway, this is, in my opinion, the most important result of the paper. The important question that remains is: Why? ….Modelling (Mühlinghaus et al., 2009; Deininger et al., 2012) provides two potential explanations: (i) the SI may be lower for the high altitude caves due to the lower pCO2 in the soil zone and (ii) precipitation rates itself are lower due to the lower cave temperature. The observed results are, thus, in perfect agreement with the modelling data. This should be mentioned and discussed in the MS.

- We agree with Scholz on the importance of the reasons why there is a trend in our data. These two points mentioned by Scholz were the two ways that we had explained our data, and we had mentioned the perfect agreement with modelling studies such as Day and Henderson (2011). However, we thank Scholz for bringing light to this point, because this important conclusion of our study is obviously not made clearly enough in the text and requires significant clarification in the revised manuscript.

p. 3627, line 20 ff.: "However, over the range of altitudes and corresponding temperatures (3–12°C) in this study, the least fractionated examples from each cave, which can be taken as those affected just by the cave temperature and only minimally by drip rate fractionation, range in values by only 1 per mill (Fig. 7c)." This is also a very important observation. For perfect equilibrium conditions, we would expect a difference of 2.25 per mill for a temperature difference of 9°C. If disequilibrium stable isotope fractionation resulted in a constant offset, we would expect the same difference in the speleothem data. However, we find a reduced difference of ca. 1 per mill. This may be explained as follows: We expect higher $\delta$18O values for the samples from high altitudes (cold

temperature), and lower values for the samples from the low altitude sites. The low altitude samples, however, show more enrichment compared to the equilibrium value due disequilibrium fractionation than the high altitude samples. This results in a reduction of the theoretically expected difference.

- We agree with Scholz that this is a very important observation and aim to explore it further in the revised text.

p. 3628, line 1: "Calcite fractionation" should be calcite oxygen isotope fractionation.

- Terminology will be carefully evaluated in the revised manuscript (General comment #3).

p. 3628, line 27: "0.25–0.5‰ fractionation in oxygen" The actual fractionation is much larger. You mean the deviation from equilibrium (see also line 29).

- As defined in the original manuscript as "fractionation" as the deviation from equilibrium calculated by Kim and O'Neil (1997), will be updated to $\Delta18O_{cc\text{-}e}$ following Feng et al. (2012) (see General Comment #3) throughout the revised manuscript. This should clarify many of the comprehension problems.

p. 3628, line 28 ff.: "However, at a poorly chosen site, the fractionation could be as large as 1.5–2 ‰ which would completely mask any low-amplitude variability and may be of a similar extent to that of the large-amplitude climate events, meaning that the significance of the oxygen isotope results would be unreliable." Or must be interpreted in another way. It may well be possible that the $\delta18O$ signal of a speleothem growing under a very slow drip may represent past variations in drip rate and, thus, be related to precipitation.

- The point that we are trying to make is that at a poorly chosen drip/stalagmite site there are too many variables affecting the oxygen isotope signal to be able to confidently narrow down the dominant factor(s) controlling the oxygen isotope record. For example, we know that the oxygen isotope signal in precipitation is affected by numer-

ous "effects" (e.g. latitude, altitude, distance in-land, amount of precipitation, surface air temperature). This is then confounded with the series of processes leading to the cave dripwater, including evapotranspiration in the soil zone and epikarst and mixing in the aquifer. Assuming latitude, altitude and distance inland remain constant, the climate signal usually desired is that of precipitation amount and air temperature or specific source effects. As the drip enters the cave, there are further confounding processes such as drip rate and ventilation that effect the $\delta$18O to various extents depending on the site chosen. At a well-chosen site, the in-cave variability can be minimised (e.g. little drip rate variations), leading to a $\delta$18O record that reflect predominantly changes in temperature, precipitation and evaporation, rather than in-cave effects. However, at a poorly chosen site these three climate signals are superimposed with isotopic signals of drip rate or other in-cave effects. In the discussion part of our paper, we explore the idea that in certain climate settings these in-cave effects boost the climate signal, whereas in other climate settings these in-cave effects detract from the climate signal. At poorly chosen sites where in-cave effects have a similar magnitude to the climate signal a highly confusing $\delta$18O signal would be produced. However, it may be possible in a case where there is minimal climate variability (e.g. during the Holocene) and in-cave effects are strong, these could be used to make an interpretation of factors such as drip rate or ventilation, which may themselves infer climatic variability. The revised manuscript will reflect this alternative interpretation possibility.

p. 3629, line 22 ff.: "During these infiltration seasons, the 18O value is lower than in summer, resulting in lower 18Odrip than the annual weighted-average rainwater value. This can be termed the weighting effect and should be quantifiable ..." Perhaps reference Wackerbarth et al. (2010) in this context, who exactly modelled these processes.

- Reference was made to Wackerbarth et al. (2012) (this issue) relating to this point, but we may also include the 2010 reference if necessary.

p. 3630, line 10 ff.: "This means that due to the geomorphological setting and rainfall trajectories predominantly from the Mediterranean, caves of the Valsugana Valley

would not be suitable for the reconstruction of palaeo-temperature changes using oxygen isotopes." I do not agree with this statement. Even if today's spatial relationship suggests almost no temperature dependence of the $\delta$18O values, the temporal relationship may show a dependence on temperature. There are so many processes involved influencing the $\delta$18O values (temperature at the source, storm tracks, changes in large scale atmospheric patterns, ...) that a $\delta$18O record from one of these caves may be suited to reconstruct temperature. At least, it cannot be excluded based on today's data.

- We are obviously aware of Scholz et al. (2012) (this issue) and how they have successfully related stable isotope variability in the record of ER76 from Valsugana Valley to NAO and solar activity during the Holocene. We would also like to take this opportunity to note that stalagmite ER76 is a particularly well-chosen site, which according to our analyses here exhibits a $\Delta$18Occ-e of 0.25‰ (at the top), that is amongst the lowest of all speleothems in the literature, thus allowing a strong correlation to climate factors with minimal influence of in-cave effects. The point that we were trying to state was that due to the unusual setting of the Valsugana valley, the altitude, and thus temperature, effect was sometimes removed from stable isotope signal. This leads to a situation whereby the absolute temperature cannot be reconstructed using speleothems from Valsugana Valley caves. However, at certain times in the past, this may not be the case due to a different trajectory from S-SW to a more westerly Atlantic provenance, minimising the shadowing effect of the Asiago plateau ridge. This was likely the case during the Holocene, and the reason for Scholz et al.'s success. We are in agreement that there are many different factors that affect the $\delta$18O values. However, Scholz appears to use this to assume that in the past the situation could have been different (and is correct in this view), but I take a more conservative view that you cannot create a robust absolute temperature record through time if you are certain that at some points in time (such as the present) the temperature-$\Delta\delta$18O correlation does not hold strong. We will add the words "robust absolute" to the sentence in question to clarify the meaning, which therefore still allows the possibility of successful NAO reconstruction from

Valsugana caves, as in the work of Scholz et al. (2012, this issue).

p. 3631, line 10 ff.: "Therefore, at well-chosen drip sites, changes in temperature associated with climate variability should be recognisable, and possibly quantifiable, in the 18O speleothem record." Again, this statement seems too strong to me (see above). It may well be that the temporal relationship is influenced by different effects than the spatial relationship.

- This statement relates to the Adige Valley to show the difference that compared with the Valsugana Valley, $\delta$18O values exhibit an altitude effect. What I think Scholz is inferring is that over time (temporal), perhaps this altitude effect could break down in the Adige Valley due to differing trajectories (spatial), leading to a situation similar to that of the Valsugana Valley. However, due to the different geomorphologies of the two valleys, the Adige being an open valley and Valsugana being a steep and narrow valley, I do not believe that this is possible. Therefore, I feel that this sentence is of adequate strength, given that it contains two words that air caution "variability 'should' be recognisable, and 'possibly' quantifiable".

p. 3632, line 23: Theoretical experiments have shown that in-cave isotopic fractionation caused by elevated temperatures and higher dripwater pCO2 would result in higher 13C values of the precipitated calcite (Mühlinghaus et al., 2009). However, such a relationship would cause the altitudinal (temperature) trend shown in Fig. 9 to shift to a more vertical slope." Note that Mühlinghaus et al. (2009) did discuss each parameter separately, i.e., kept the other parameters constant. This is particularly important for cave and soil pCO2, which is not constant for the monitored caves. Thus, the mentioned effect may well be already contained in the monitoring data.

- In the revised manuscript, we plan to make a more detailed evaluation of 13C isotope values using a two end-member model (atmospheric and soil CO2). This should make our interpretations clearer and allow better comparisons to the modelled data.

p. 3633, line 1 ff.: Be cautious with "forced degassing" (see general comment)

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- All terminology will be updated (see general comment #3).

p. 3634, line 11 ff.: "... a decrease in the amount of oxygen isotope fractionation with a reduction in temperature ..." As it stands, this statement is wrong. You mean the deviation from the expected value ...

- "Amount of oxygen isotope fractionation" will be replaced with $\Delta$18Occ-e (see general comments).

p. 3634, line 21 ff.: "caves where the oxygen isotope composition is dominated by rainfall changes through the amount effect, such as those in monsoon regions (e.g. Wang et al., 2001) ..." Although it is not important for the discussion and I perfectly agree with the general conclusions, it may be worth to mention that there is increasing evidence that the Chinese speleothem records do not reflect changes in rainfall amount (Pausata et al., 2011).

- Yes, although slightly off topic, it may be worth mentioning this reference.

p. 3636, line 6 ff.: "... shorter time for degassing at the stalactite tip." This is not correct (see above).

- This will be changed to rapid precipitation (see general comment #1).

Conclusions: It appears to me that this section mainly repeats the discussion from the previous section. I would either merge the two sections or substantially shorten the conclusions.

- We will aim at shortening the conclusions and avoiding undue repetition.

We sincerely thank Denis Scholz for his detailed and highly constructive review that will significantly improve the quality of the final manuscript. We thank you for painstakingly correcting all the terminology, isotopic processes and suggesting useful references.

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