Clim. Past Discuss., 8, C1846–C1856, 2012
www.clim-past-discuss.net/8/C1846/2012/

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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: 9 October 2012

"Monitoring stable isotopes in caves over altitudinal gradients: fractionation behaviour and inferences for speleothem sensitivity to climate change"

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Manuscript Number: cpd-8-3613-2012

This study presents an isotopic dataset obtained from rainwater and associated cave dripwaters and calcites over a steep elevation gradient in the Alps. The relationships between elevation, temperature, and calcite isotopic composition are examined over a large range in temperatures (3 $\sim$ 12°C); observations that would be very difficult to carry out within one single cave. This range in temperature is then considered to be a proxy for glacial-interglacial transitions, and trends from multi-cave regression lines are used to predict the general behavior of calcite isotopes during extreme climate change. The data presented have the potential to elucidate features of the ongoing debate in the cave paleoclimate community about equilibrium/disequilibrium fractionation and the relative effects of each forcing mechanism on cave calcite – especially useful at lower temperatures where not much modern calcite data exists in the literature. The approach to that end is good, and I would like to see this manuscript published. But there are several key features of the paper that should be further developed prior to publication.

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 with the bulk of current literature. Since one of the central themes of the paper is process effects on calcite isotopic composition (i.e., temperature, ventilation, drip rate) over a range of elevation I would suggest the authors include one paragraph outlining – in detail – the sources and magnitude of fractionation in the cave system. This paragraph should include groundwater-bedrock systematics (see Frisia et al., 2011; Lambert and Aharon, 2011) and in-cave degassing and subsequent precipitation systematics (see Dreybrodt and Scholz, 2011) for both carbon and oxygen isotopes. This paragraph should be introduced prior to discussion of the data. 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.

2. There are several instances where pCO2 (aq) degassing is noted as the cause for a shift in calcite isotopic composition, however the systematics of degassing, supersaturation, and precipitation is not addressed in any detail. 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. I suggest the authors include a brief discussion of saturation state and precipitation rate in light of the most relevant theoretical and laboratory results (Dove et al., 1992; Teng et al., 2000; Weidner et al., 2008; DeYoreo et al., 2009; Dietzel et al., 2009; Scholz et al., 2009; Polag et al., 2010; Dieninger et al., 2012). I would also suggest that the authors provide the saturation state information in Table 2 and figures comparing SI to elevation, drip rate, and deviation from expected equilibrium fractionation.

3. The site descriptions and snapshot sample data presented are adequate to draw broad conclusions about calcite isotope behavior. But I the important connections between soil pCO2/ δ13C, dripwater DIC/δ13C, cave air pCO2, calcite δ13C 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’ pCO2 values. It should be clear to the reader how these ‘expected’ values were estimated.

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.

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 those two endmembers.

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

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authors refer?

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. Collecting snapshot data essentially ensures that annual variability cannot be accounted for and therefore the data presented are subject to relatively large uncertainties. This is especially true for caves that have large dripwater reservoirs with long transport time, and for caves that exhibit strong seasonal changes in ventilation.

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.

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. 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

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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.

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?

p. 3625; line 3: "With elevated temperatures, and also slower drip rates, the same experiments also found that the δ18Ocalcite 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).

p. 3625; line 16: "The fractionation amount has then been computer as the difference between the expected δ18Ocalcite and the δ18Ocalcite measured on the cave precipitates". - The difference between predicted δ18O and measured δ18O 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$18Ocalcite, or more specifically in 1000 ln α notation). This should be modified here and throughout the manuscript, including lines Figures 7 and 8.

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.

p. 3626; line 5: "It likely signifies that within the vados 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.

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.

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, Tremain et al. (2011) demonstrated ventilation and temperature driven seasonal variations in δ18Ocalcite of ± 1.5‰ and seasonal variation δ13Ccalcite of up to ± 2.5‰ under quasi constant drip rate conditions.

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.

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?

p. 3633; line 13: “Calcite from Bigonda Cave (BG) consistently shows higher δ13C 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 pCO2. The δ13C signal is picked up from where the water infiltrates the bedrock, which according to Fig. 9a is around 1000 m a.s.l.” - Calcite δ13C 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‰, resulting in DIC of around -11‰ and ventilation-driven CO2 degassing enrichment of +2 to +5‰ to around -8‰

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in calcite. This result may not directly comparable to high-altitude caves because the proportions of soil-gas CO2 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-soilgas-bedrock-DIC fractionation system as outlined by Lambert and Aharon (2011).

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 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.

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 δ18O cannot be accounted for by rainfall amount, and are probably due to source effects (see Clemens et al., 2010; Pausata et al., 2011).

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 δ18Ocalcite . If so, this passage should be modified accordingly.

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 δ18O 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 δ18O 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. Frisia, S., Fairchild, I., Fohlmeister, J., Miorandi, R., Spötl, C., Borsato, A., 2011. Carbon mass-balance modelling and carbon isotope exchange processes in dynamic caves. Geochim. Cosmochim. Acta 75, 380-400. Lambert, W., Aharon, P., 2011. Controls on dissolved inorganic carbon and δ13C in cave waters from DeSoto Caverns: Implications for speleothem δ13C assessments. Geochim. Cosmochim. Acta 75, 753-768. Kim, S. T., O'Neil, J.R., 1997. Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. Geochim. Cosmochim. Acta 61, 3461-3475. Dreybrodt, W., Scholz, D., 2011. Climatic dependence of stable carbon and oxygen isotope signals recorded in speleothems: From soil water speleothem calcite. Geochim. Cosmochim. Acta 75, 734-752. Dove, M. T., Winkler, B., L., M., Harris, M.J., Slaje, E.K.H., 1992. A new interatomic potential model for calcite: applications to lattice dynamics studies, phase transition, and isotope fractionation. American Minerologist 77, 244-250. Teng, H., Dove, P., De Yoreo, J., 2000. Kinetics of calcite growth: surface processes and relationships to macroscopic rate laws. Geochim. Cosmochim. Acta 64, 2255-2266. Wiedner, E., Scholz, D., Mangini, A., Polag, D., Mühlinghaus, C., Segl, M., 2008. Investigation of the stable isotope fractionation in speleothems with laboratory experiments. Quat. Int. 187, 15-24. Dietzel, M., Tang, J., Leis, A., Kohler, S. J., 2009. Oxygen isotopic fractionation during inorganic calcite precipitation - Effects of temperature, precipitation rate and pH. Chem. Geol. 268, 107-115. De Yoreo, J., Zepeda-Ruiz, L., Friddle, R., Qiu, S., Wasylenki, L., Chernov, A., Gilmer, G., Dove, P., 2009. Rethinking classical crystal growth models through molecular scale insights: consequences of kink-limited kinetics. Cryst. Growth Des. 9, 5135-5144. Polag, D., Scholz, D., Mühlinghaus, C., Spötl, C., Schroder-Ritzrau, A., Segl, M., Mangini, A.,

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Jour. Hydrol., 409, 682-695 Clemens, S. C., Prell, W. L., Sun, Y., 2010. Orbital-scale timing and mechanisms driving Late Pleistocene Indo-Asian summer monsoons: Reinterpreting cave speleothem δ18O. Paleoceanography VOL. 25, PA4207, 19 PP., doi:10.1029/2010PA001926

Please also note the supplement to this comment:
http://www.clim-past-discuss.net/8/C1846/2012/cpd-8-C1846-2012-supplement.pdf

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