

***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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Review of the manuscript “Monitoring stable isotopes in caves over altitudinal gradients: fractionation behaviour and inferences for speleothem sensitivity to climate change” by Johnston et al., submitted to Climate of the Past

General comment:

This paper presents cave monitoring data from eight caves located in steep altitudinal topography in the Italian Alps. The different climate and cave parameters of the cor-

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responding caves enable to study the effect of temperature, soil and cave pCO₂ and drip rate on drip water and speleothem stable isotope values and, thus, the underlying isotope fractionation processes.

The basic idea is good, the presented data are interesting and although most data were sampled during a single month and the data set only represents a very short snapshot in time, some general conclusions can be drawn from the data. The manuscript is, thus, definitely suitable for publication in the CP special issue on speleothems.

However, I have three general comments that should be taken into account before I can recommend publication:

1. The description of the processes occurring inside the cave and on the speleothem surface (degassing of CO₂, establishment of supersaturation with 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.

There is still confusion in the speleothem community about the origin of non-equilibrium stable isotope fractionation in speleothems. In particular, “rapid” or “forced degassing” of CO₂ is often offered as an explanation for observed disequilibrium. However, recent papers (Dreybrodt and Scholz, 2011; Dreybrodt, 2011) have clearly described and modelled the different processes and their corresponding characteristic time scales.

The infiltrating water first equilibrates with the high pCO₂ in the soil zone and subsequently dissolves CaCO₃ until it is saturated with respect to calcite. When it enters the cave, where pCO₂ is usually lower, the surplus CO₂ degases and supersaturation is established. Degassing of CO₂ from thin films is always fast (i.e., on the order of seconds, Dreybrodt and Scholz, 2011). This results in an increase in the d¹³C value of the DIC (Dreybrodt and Scholz, 2011), but has no effect on speleothem d¹³C and d¹⁸O values because calcite precipitation starts after supersaturation has been established. Subsequently, calcite precipitation starts, and even if precipitation occurs in

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isotopic equilibrium (actually all available models use equilibrium fractionation factors), the associated Rayleigh fraction process results in an increase of the d13C and d18O values of the DIC during precipitation. This increase may also be visible in the d13C and d18O values of speleothem calcite (Dreybrodt and Scholz, 2011; Mühlinghaus et al., 2009; Scholz et al., 2009; Dreybrodt, 2008). If precipitation is fast (e.g., in case of a high degree of supersaturation), the increase and, thus, the deviation from isotopic equilibrium will be larger than if supersaturation is relatively low. Consequently, it is not rapid degassing but rapid precipitation, which results in disequilibrium stable isotope values in speleothems.

This needs to be clarified throughout the MS.

2. All the above mentioned processes have been described in detail and modelled in recent publications (Deininger et al., 2012; Dreybrodt and Scholz, 2011; Mühlinghaus et al., 2007, 2009; Scholz et al., 2009; Dreybrodt, 2008; Dreybrodt, 2011; Romanov et al., 2008). Most of these studies have been performed in the framework of the DAPHNE research group. As the paper is intended to be published in the corresponding special issue, it is surprising that most of these papers are not referenced. These papers must be discussed and cited.

The same is true for other experimental (Polag et al., 2010; Wiedner et al., 2008) and modelling work (Wackerbarth et al., 2010) of DAPHNE related to the discussion of the paper.

3. In some parts of the MS, the language is not precise enough, in particular the discussion of stable isotope fractionation.

For instance, the authors state that “oxygen isotope fractionation was found to decrease in cooler caves” (p. 3637, line 2). This is not correct. In general, isotope fractionation is larger for cooler temperatures. This is clearly visible in Fig. 7D. However, the deviation from the value expected under equilibrium isotope fractionation conditions is lower for cooler temperatures.

This must be corrected throughout the MS.

Specific comments:

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

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

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

p. 3618, chapter 4.1: Is the saturation index available for the drip water? This would be of great importance because, as discussed above, isotope fractionation depends on the precipitation rate, which, in turn, is driven by the degree of supersaturation. This parameter is, thus, even more important for isotope fractionation than cave pCO₂. It would be great to see a plot of SI vs. altitude.

p. 3619, chapter 4.2: It would be interesting to see how the regional d18O and dD data compare with the Global Meteoric Water Line.

p. 3620, line 23 ff.: “Therefore, in the following discussion, the least fractionated example from each cave ...” It appears to me from Fig. 6 that the sample with the lowest d13C value has been used even if its d18O value is higher than that of another sample. Which d18O value has been used in this case? Please clarify.

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?

p. 3622, line 25 ff.: “... since there is a strong correlation between the saturation state of dripwaters and the altitude ...” Again, if these data are available, it would be very interesting to show them in this paper and discuss their effect on stable isotope fractionation.

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

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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.

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.

p. 3623, line 24 ff.: “... although modification of the original dissolved inorganic carbon (DIC) ¹³C, by degassing at the stalactite tip, cannot be excluded.” Initial degassing of the surplus CO₂ after entering the cave, necessarily results in an increase of the d¹³C value of the DIC (Dreybrodt and Scholz, 2011). However, as explained above, this effect is not visible in the precipitated speleothem calcite.

p. 3624, line 15 ff.: The reference of Scholz et al. (2012) can be updated as the paper has meanwhile been published in CP.

Chapter 5.3: The discussion of the petrography is interesting. However, as these data seem not to be available for all caves and the following discussion is mainly based on temperature and pCO₂, this section may be shortened.

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.

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. Nevertheless, the authors may be right in this point. In order to corroborate this statement, they may briefly discuss previous publications, which came to a similar conclusion (Tremaine et al., 2011), here.

p. 3626, line 11 ff.: “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

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surface, where it could undergo CO₂ degassing that cause the isotopic disequilibrium.” As stated above, this statement is wrong! There is simply more time for precipitation of calcite. The deviation from the equilibrium value does not result from degassing or kinetic fractionation but only from the ongoing Rayleigh distillation during precipitation (Scholz et al., 2009; Mühlinghaus et al., 2009).

p. 3626, line 14 ff.: “In a drier climate, evaporation of the dripwater must also be considered. However, here the relative humidity of the caves was always higher than 90% ...” 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.

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

p. 3626, line 23 ff.: “...there is a trend towards less fractionated ¹⁸O calcite with higher altitude, and thus lower temperatures.” I guess you mean less deviation from equilibrium rather than less fractionation. Anyway, this is, in my opinion, the most important result of the paper. The important question that remains is: Why? As explained above, the degree of observed isotopic disequilibrium depends on the interplay between calcite precipitation and drip rate. If precipitation is rapid and the drip rate is low, a large degree of disequilibrium is expected. If we observe only a slight deviation from equilibrium, as is the case for the high altitude sites, we require relatively slow precipitation. Modelling (Mühlinghaus et al., 2009; Deininger et al., 2012) provides to 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.

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

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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 d18O 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.

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

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).

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 d18O signal of a speleothem growing under a very slow drip may represent past variations in drip rate and, thus, be related to precipitation.

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.

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 oxy-

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gen isotopes.” I do not agree with this statement. Even if today’s spatial relationship suggests almost no temperature dependence of the d18O values, the temporal relationship may show a dependence on temperature. There are so many processes involved influencing the d18O values (temperature at the source, storm tracks, changes in large scale atmospheric patterns, ...) that a d18O record from one of these caves may be suited to reconstruct temperature. At least, it cannot be excluded based on today’s data.

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.

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.

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

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 ...

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).

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

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.

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