

Anonymous Referee #1

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Van Rampelbergh and co-authors report detailed data from a regular cave monitoring campaign from Han-sur-Lesse cave in Belgium. The campaign in this show cave was conducted from November 2012 to January 2014. Each two weeks they obtained data for various cave parameters as temperature (atmospheric, cave and drip water), meteoric rain, cave air pCO₂ and stable isotopes (of CO₂, dissolved inorganic carbon and carbonate). The monitoring data were adequately discussed. The discussion was lead with the aim to understand the variations of the oxygen and carbon isotopic composition of recently - on glass plates - precipitated calcite and from one short but fast growing part of a stalagmite from this cave system. The data are new and essential to understand cave related processes, which is necessary to interpret time series of stalagmite stable isotope proxies in terms of climate variations. The paper is well written and structured. The discussion is clear and for most parts solid. (Please find more information about this in the 'specific comments' section.) Finally, to my opinion, the data support the final interpretation. Therefore, I think that this paper meets the publishing criteria for *Climate of the Past*. The paper should be published in CP after implementation of a few modifications and addressing the points raised below.

Specific comments

Han-sur-Lesse cave is a famous show cave. I guess that several thousand visitors per year go through the whole cave system. Such large number cannot be neglected for the cave atmosphere. They all respire CO₂, for example. This might have an impact on the measured cave parameters and should be discussed. For example, during summer the number of visitors is certainly higher than in autumn or winter. This introduces maybe some artificial seasonality to the cave system (T, cave air CO₂ and δ¹³C). I feel that a discussion of this aspect is necessary within this paper.

Indeed, as correctly mentioned by the reviewer, the Han-sur-Lesse cave has several thousand visitors during the whole year with the high season lasting from April to September. Although large numbers of visitors pass through the cave every day, we expect the effect of the visitors on the measured parameters to be negligible due to the size of the cave chamber. With a height of 60m and a width of 150m good for a total volume of 124 000 m³ and a river flowing at the bottom of the chamber causing good air mixing, the effect of visitors is negligible. This assumption has been confirmed with a test carried out at the beginning of the monitoring campaign. The reported parameters were measured before the first tourists entered the cave and after several groups passed by the speleothem location. No significant difference could be measured confirming that visitors do not influence on the cave parameters. To be sure that the measured parameters are reflecting the natural conditions as close as possible and to do a consistent measurement campaign, the cave parameters were always measured around 9 AM before the visitors are entering the cave.

We understand that this discussion point should be clarified, we added the following paragraphs:

Methods P1826 L28: "To make sure that the measured parameters are closely reflecting the natural conditions and to guarantee a consistent measurement campaign, the cave parameters were always measured around 9 AM before the first visitor enters the cave. To investigate the visitors possible influence on the measured cave parameters, a test was carried out by measuring these parameters before visitors were allowed into the cave and after the passage of different groups."

Results P1829 L19: "No difference in the measured cave parameters is observed before the start of the visits and after a large number of visitors have entered the chamber."

Discussion P 1833 L 19: "A large number of visitors enter the cave and the Salle-du-Dôme chamber every day. The studied Salle-du-Dôme chamber has a height of 60m and a width of 150m good for a total volume of 124 000 m² and a river flowing at the bottom of the chamber causing good air mixing. Due to the large size and the good ventilation of the chamber, the effect of the visitors on the measured parameters is expected to be negligible. This was confirmed by a series of tests, where similar cave parameter values were measured before and after groups visited the chamber. For the Salle-du-Dôme chamber, we consider the measured values to reflect the natural conditions of the cave atmosphere."

In addition, I think that the characteristics of the Lesse River are also underrepresented in the discussion of this paper. Cave temperature might be not only influenced by mixing with outside air induced by the river (P 1833, l 22). In addition, the water of the river might transport a lot of energy from outside (gained before it enters the cave) to the inner cave. This heat might then be released in the cave with more impact in the warm months than in the cold.

We fully agree that the river flowing at the bottom of the chamber must have an influence on the temperature of the Salle-du-Dôme. Since we do not have a temperature record of the river water we cannot quantify this effect. We added the following paragraph on P 1833 L21 to explain this:

"Apart from the influence of the external temperature, the temperature regulation of the Salle-du-Dôme chamber is probably also influenced by the Lesse river flowing at the bottom of the chamber. Due to the water flow, a good mixing of the cave air is induced causing the outside air to enter the cave chamber more easily. In addition, the water of the river transports energy from the outside (gained before it entered the cave) to the inner cave. This heat can then be released in the cave with more impact in the warm summer months than in the winter months. Since no temperature record of the river is available, the effect of the Lesse river on the cave air temperature cannot be quantified."

Another point is that I would like to read a few words about prior calcite precipitation and if it is important for this site (e.g., is there a big or small stalactite above the stalagmite or is there other evidence). Unfortunately nothing is mentioned in the text about this effect. However, this would provide a better overview about the cave system and cave related processes.

We agree that it can be interesting for the reader to have information on PCP of the studied site. Therefore we added the following paragraph on P 1829 L 16 at the beginning of the results part: *"The drip water feeding the Proserpine falls from a small drapery-shaped stalactite indicating that only a small part of the dissolved calcite precipitates from the drip water when hanging on the ceiling of the cave. The drip falls for approximately 30 m before reaching the surface of the Proserpine. The Proserpine grows under a 'flow' or continuous 'rain' that falls on the surface of the stalagmite at 4 points. The core used in this study was sampled in the center of the speleothem, where water is dripping on the stalagmite during the whole year."*

While the previously mentioned comments might be regarded as additional information, which are helpful for the reader to understand the cave system, I think that the discussion about the seasonally varying pH needs to be more precise and redirected (P 1834, l 17 and the whole paragraph). In fact, I think the whole discussion about the pH is not correct. The reason, why I think like that is the following. I agree with you completely that the cave drip water is well mixed throughout the year, as indicated by the relatively constant drip water d18O and dD compared to the isotopic composition of the precipitation. However, I do not see the point, why the pH value, which certainly varies in the soil with the seasonally variable soil air pCO₂, should not be affected by this mixing process. Either the water is well mixed before entering the cave and there is no difference in all the chemical parameters, or it is not. Since, CO₂ dissolution in the soil and CaCO₃ dissolution in the karst are believed to be rather fast processes (E.g., Dreybrodt and Scholz, GCA, Vol 75, p 734 - 752, 2011), at least if compared to the water mixing time above Han-sur-Lesse cave, and hence occur mainly in the upper part of soil-karst-system, those processes should not be important for variations in the drip water pH. To my opinion, it is a better concept to accept the well mixed water reservoir above the cave and assume more or less constant values year-around for the various parameters of drip water before entering the cave. Then another process is necessary for the variations in the pH values. I think that the cause of this pH variation is due to a variable amount of degassing of CO₂ from the drip water. The amount of CO₂ degassing is a function of cave air CO₂. The amount of cave air pCO₂ would define the maximum amount of CO₂, which is able to degas. The lower the cave air CO₂, the more CO₂ can degas from the solution resulting in a higher pH of the water. This process is slightly modulated by drip rate, since with fast drip rates it is possible that complete CO₂ degassing is not achieved due to a too fast succession of following drops. Therefore the expected anti-correlation between cave air pCO₂ and drip water pH is not expected to be perfect. P 1838, l 8: You wrote that d13C of dissolved inorganic carbon does not show a seasonal cycle. Well, I would say, that one can have another opinion about this issue.

There is also a quite good reason, why the annual cycle might be visible although the water is well mixed. If indeed the degassing of CO₂ drives the pH variation, then this degassing affects also the d13C of the DIC in drip water. More degassing during periods of low cave air pCO₂ would result in a larger loss of preferentially light C isotopes. Hence the d13C of DIC is expected to be less negative during periods of low cave air pCO₂ - as it is observed.

We are very thankful to the referee to have made this suggestion of the $p\text{CO}_2$ influencing the drip water pH. We absolutely agree that this effect is most probably the driving factor behind the seasonal pH variations in the drip water. Therefore we reworked the concerning paragraph (P 1834 L 17 and whole paragraph). We also agree that there is a rather small seasonality in the drip water $\delta^{13}\text{C}_{\text{DIC}}$ that also related to the CO_2 -degassing of the drip water when it enters the cave. Therefore we reworked the whole paragraph on P 1834 L 17 to the following: *"The drip water pH clearly displays a seasonal variation that is interpreted to be related to the seasonally varying cave air $p\text{CO}_2$. In winter, when the $p\text{CO}_2$ is low, more CO_2 will degas from the drip causing the pH of the drip water to increase. The effect of CO_2 -degassing on the pH can slightly be modulated by the drip rate. During periods of extremely high drip rate, full CO_2 -degassing cannot be completed. The drip water will therefore be lower in pH during strong drip flow events. This is exactly the case during the May wet event of 30 May 2013, where the discharge peaks to high values and where the pH (Fig. 2f) drops from 8.2 to 7.9."*

We also added the discussion of the seasonally changing $\delta^{13}\text{C}_{\text{DIC}}$ below this paragraph on P 1834 L 17: *"More degassing of the drip water due to low cave air $p\text{CO}_2$ also results in the preferential loss of light C-isotopes. This will cause the $\delta^{13}\text{C}_{\text{DIC}}$ in the remaining drip water to be more positive during periods of strong degassing such as is the case in winter. This effect on the $\delta^{13}\text{C}_{\text{DIC}}$ is rather small but visible in the monitoring results with slightly more positive values during winter."*

Technical corrections

P 1825 l 11: isotope -Adapted

P 1826 l 7: Please, delete 'in' after 'heavy' -Adapted

P1827, l 2-3: Is it likely that water temperature adjusted itself to the room temperature, while stored in the pool on top of the stalagmite? That would mean the water temp was initially somewhat colder during penetration to the cave. The temperature of the water was measure in a small pool on the stalagmite surface. Not the big inflatable pool used to collect the water and determine the drip flow. There is also a constant drip falling in that small pool refreshing the water continuously. Therefore we think that the water temperature is not equilibrated with the cave air temperature. To clarify this the following sentences were added on P 1827, L2: *"The drip water temperature and pH were determined in a small pool (6 cm wide and 3 cm deep) formed on the stalagmite's surface where drip water is continuously falling in. The extremely short residence time of the water in this small pool guarantees that the temperature and pH suffer minimal alteration."*

P 1828, l 22: I guess 'evaporation' is not the right word here. Instead, I suggest using the term 'diffusion'. This is probably, what you meant. -Adapted

P 1830, l 2: remove the '.' in front of 'in early June'. -Adapted

You mention your present Figure 5 (P 1831) before Figure 4 (P 1840). Please change this accordingly.

We thank the referee for this comment and changed the numbering of the pictures. Figure 4 became figure 5, and figure 5 became figure 4. Figure captions and text were adapted to this change.

P 1832, l 8: 'These drops do not:::' -Adapted

P 1833, l 8 and 13: In these lines you stated that the delay is five to six months. However in Fig. 3 you wrote the delay is 4 months. Please clarify this and be consistent.

We thank the referee for pointing out this inconsistency. We changed the text in figure 3 to "5 to 6 months residence time of the water in the epikarst".

P 1833, l 20: Here you state that the mean cave air temperature is about 1 C warmer than the mean drip water temperature. A few pages before the offset was only 0.5C (P1829, l 24). Please clarify this and be consistent.

We thank the referee for this comment. The correct difference in temperature between the drip water and the cave air is 0,5°C. However, following the comments of reviewer 2, the last part of the sentence was removed so no temperature difference is given anymore.

P 1838, l 2: I suggest to delete the text in the brackets. This gives no additional information. -Adapted

P 1838, l 5-6: To be more precise, I think you should rephrase your point (ii). The fractionation factors are indeed important for the $\delta^{13}\text{C}$ composition of the carbonate, but those factors are mainly driven by temperature in this pH range.

We thank the referee for this comment and we adapted point (ii) to: 'The $\delta^{13}\text{C}$ composition of calcite deposited in equilibrium with its drip water depends on (i) the $\delta^{13}\text{C}$ composition of the Dissolved Inorganic Carbon (DIC) in the drip water and (ii) the temperature dependent fractionation factor between the DIC and the deposited calcite for a pH range around 7.'

P 1838, l 21: Do you mean 'disequilibrium'? -Adapted

P 1838, l 29: 'stronger' should be included before 'enrichment', because an enrichment in $\delta^{13}\text{C}$ is all the time observed, no matter how large the pCO_2 difference is. -Adapted

P 1839, l 21: 'CO₂ degassing is more important'. As I understood the theory in the cited papers your argumentation is not completely true. CO₂ degassing is all the time really fast and has only a minor effect on the final $\delta^{13}\text{C}$ of precipitated CaCO₃ (see for example Dreybrodt and Scholz, 2011). It is the CaCO₃ deposition, which has more time, with a slower drip rate. This process in addition to the typical characteristics of a Rayleigh fractionation is responsible for higher $\delta^{13}\text{C}$ values in precipitated calcite.

We do not agree with this comment. Indeed, CO₂-degassing occurs immediately after the drop reaches the ceiling of the cave. This process always happens

immediately when a drop enters the cave atmosphere. For all cave sites, the degassing is fast due to the pCO₂-difference between the epikarst and the cave air. However CO₂-degassing also continues after the first degassing event when the drop entered the cave. This process is enhanced when less drip water feeds the stalagmite causing a long residence time of the water film covering the stalagmite surface. When the process of 'CO₂ degassing' is discussed in the paper, it is exactly this degassing after entering the cave that we mean.

Furthermore the argument that a longer residence time causes the calcite to become heavier is incorrect. The process acts in the opposite way. According to the Rayleigh distillation, the heavy isotopes precipitate preferential from the solution. The lighter C-isotopes will only precipitate in a later stage. Leaving the solution for a longer time on the stalagmite surface, and considering that no evaporation occurs, the deposited calcite must thus become lighter. Since we observe that lower drip rates correspond to heavier calcite, this process cannot be present.

P 1839, l 21: Please delete one of the two 'in'. -Adapted

P 1839, l 25: Please, replace 'evaporation' by 'degassing'. No phase transition between liquid CO₂ and gaseous CO₂ occurs. It is a degassing from dissolved C to gaseous CO₂. -Adapted

P 1841, l 17-22: From the theory, this is fine, but you did not show the according carbonate concentration data which would indicate that your argumentation is right. And if you assume that your water is well mixed before it arrives the cave the carbonate ion concentration should be more or less constant. However, as the drip water comes into contact to the cave air prior calcite precipitation might occur, which would change the carbonate ion concentration.

We agree with the referee that this paragraph needs to be reworked. As already suggested in the specific comments, it is not the residence time of the water in the epikarst that influences the seasonality in the chemical parameters of the Proserpine drip water such as pH, $\delta^{13}\text{C}_{\text{DIC}}$ or dissolved ions, but rather seasonally varying in-cave processes such as the amount of CO₂-degassing. Since referee 2 also commented on this paragraph, the whole interpretation of the factors influencing the growth rate of the Proserpine has been rewritten. The new paragraph, where we explain that more data is necessary in order to understand the influence of carbonate concentration on the deposition rate, is the following (P1841 L 15-27): *"The very compact and dark structure of the summer layers compared to the porous structure of the winter layers consequently indicate that the growth rate also varies seasonally. Different factors such as drip rate, amount of dissolved carbonate ions or amount of CO₂ concentration in the cave atmosphere affect the growth rate of speleothems. In the case of the Proserpine, the strong seasonal difference in drip rate between summer and winter is supposed to be the main driver of the seasonality in growth rate. The high discharge in winter leads to an increase in growth rate and causes the formed calcite to be porous and full of small inclusions. The CO₂ concentration of the cave air is also influencing the calcite deposition rate of the Proserpine. Low cave air pCO₂ in winter leads to stronger degassing of the drip water and consequently to an increase in the deposition rate of the calcite. Both effects, the drip rate and the pCO₂, act in the*

same direction and cause the calcite to be deposited faster in winter compared to summer. Other factors such as the amount of dissolved carbonate in the drip water are most probably also having an influence on the Proserpine growth rate with an increase in calcite deposition rate when the concentration of carbonate dissolved ions in the water is higher. This link has clearly been observed in the drip waters from the Père Noël cave (Genty and Deflandre, 1998). Further investigation in the seasonal cycle of the carbonate dissolved ion concentration of the Proserpine drip water is necessary to understand its influence on the calcite deposition rate."