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Interactive comment on "Subaqueous speleothems (Hells Bells) formed by the interplay of pelagic redoxcline biogeochemistry and specific hydraulic conditions in the El Zapote sinkhole, Yucatán Peninsula, Mexico" *by* Simon Michael Ritter et al.

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Author′s Response to the Interactive comment on "Subaqueous speleothems (Hells Bells) formed by the interplay of pelagic redoxcline biogeochemistry and specific hydraulic conditions in the El Zapote sinkhole, Yucatán Peninsula, Mexico" by Simon Michael Ritter et al.

The authors are very grateful for the time and effort taken for reviewing the manuscript

in detail and appreciate the constructive comments and suggestions by anonymous referee #2. We addressed all issues raised by the referee in a point by point response below.

Referee′s general comment: This paper presents detailed hydrogeochemical and geochemical analyses of the water column and the so-called Hells Bells formed in a cenote on the Yucatan Peninsula, Mexico, in order to determine the processes leading to the development of the Hells Bells. This is an interesting topic because these submerged speleothems are a unique feature suggesting that their growth is only possible in case of very specific conditions.

The paper is, in general, well written, the results are clearly presented and the developed hypotheses are sound and justified by the data. The text is here and there a bit lengthy (in particular, the conditions leading to the formation of the Hells Bells are repeated several times), but this is not a major issue.

I have two (moderate to major) general comments that should be addressed by the authors prior to publication. The first – and more serious - comment is related to the changes in the depth of the halocline, which are considered as the reason resulting in growth of Hells Bells at different water depths or of large bells over a longer time. The authors develop a hypothesis that the depth of the halocline is related to fresh water recharge at the surface and even suggest a potential relationship with the occurrence of hurricanes. However, the time scale of the growth of the Hells Bells is not discussed with sufficient detail in the paper. Considering the enormous size of at least some of the bells, it is hard to believe that these should have developed due to seasonal or episodic changes in the depth of the halocline. I would rather believe that this requires a longterm shift in the depth of the halocline, for instance over several thousand years during the Holocene. I had a quick look at the previous paper of the same group (Stinnesbeck et al., 2017b), which presented a few U-series data and reported growth rates of ca. 10-100 μm/a. In case of such slow growth rates, it is hard to believe that a short-term decrease in the depth of the halocline due to a recharge event would have a visible effect. In contrast, growth of a really large bell, requires slow and progressive changes in the (mean) depth of the halocline. The U-series ages ranging from a few hundred to a few thousand years reported by the previous paper, actually seem to confirm this. Thus, the authors should ideally present many more U-series data trying to resolve the timing and duration of the growth of the Hells Bells. If this is technically impossible or beyond the scope of the paper, they could also present data from a second campaign, probably shortly after a major recharge event. As far as I understand, these measurements are currently conducted (p. 26, line 30ff.) and could easily be included in a revised paper. If the authors do not want to include additional data (neither U-series, nor elevation data of the halocline), they must clearly address this issue in the revised paper and critically discuss the time-scales of the dynamics of the halocline and the growth rates of the Hells Bells.

Response: We fully agree that growth rates should be discussed in the MS and followed the referee′s suggestion by critically discussing and estimating Hells Bells growth rates. We address this issue in a new chapter in the revised MS (Section: "4.3.1 Calcite precipitation rates"). Concerning the presentation of additional data, we are currently working on the Hells Bells from different angles and produced an amount of data that cannot be shown in one manuscript only. Manuscripts, also addressing age-dating of Hells Bells, are currently in preparation. We conducted a second campaign which confirmed the data presented in the MS, but the major goal of second campaign was to study other cenotes showing Hells Bells and compare them to a cenote without Hells Bells. We are currently preparing a manuscript presenting these data. Additionally, as the dynamic halocline elevation was also of major concern for Anonymous referee #1 and we already addressed a lot of the raised issues and we would therefore also like to refer to the Author′s response AC1 (https://www.biogeosciences-discuss.net/bg-2018-520/#discussion).

Referee: My second point concerns the typical bell-shape of the Hells Bells. In section 4.3.2, the authors discuss several processes, but none of the them – as far as I

understood – explains the "conically divergent" (p. 27, line 14) shape of the bells. This issue should either be addressed more clearly, or it should be stated in the MS that the processes discussed in the text cannot completely explain the typical shape of the bells.

Response: Absolutely correct, we did not comment on the conical divergent shape of Hells Bells but of course we thought about that, too. We think that the conical shape of Hells Bells and their downward divergence could be the macroscopic expression of the calcite crystal′s microscopic features. We observed two major phases of calcite crystals, blocky or mosaic and elongated doog-dooth calcites. The latter are arranged in a botryoidal structure which strongly resembles the shape of the larger Hells Bells structures. We added this observation into the discussion section 4.3.2 and added a thin section photograph showing such features to the supplement (Fig. S4 in the revised Supplement). Preferential or faster growth on the outer edges of Bells, especially the edges pointing towards the center of the cenotes (this is described in detail in section 4.3.2) may lead to the hollowness because once these outer edges of a specimen have grown slightly deeper that the rest of the specimen, then the net growth of these parts will be higher because it is more frequently reached by the zone of calcite precipitation. This would ultimately lead into the observed hollowness of the larger specimen of Hells Bells. We also integrated these thoughts on the Hells Bells features into the manuscript in section 4.3.2

Referee: In summary, although the paper is generally very interesting and well written, and the data clearly deserve publication, I can only recommend publication in Biogeosciences after revision. Below, I list a few additional, more detailed comments.

Referee′s detailed comments:

Referee: Page 6, line 9: Why are only data from a single campaign reported? In particular considering the important aspect of the dynamics of the halocline (see above), it would be much better to provide at least a few data from an additional campaign conducted shortly after a major recharge event (hurricane).

Response: We installed data loggers in the cenote for permanent observation of the halocline elevation and water level. This data is so far ($\sim$1 year) very promising, however there was no major precipitation event like a since the start of the measurement in December 2017. We elaborated this issue in our response to Referee comment #1 (AC1 on pages C2–C3 https://www.biogeosciences-discuss.net/bg-2018-520/#discussion). Furthermore, the main goal of this study is to present detailed hydrogeochemical results in order to develop a hypothesis on the mechanism for subaqueous calcite precipitation. The aspect a halocline elevation is a direct consequence of the conclusion that calcite most likely precipitates within the narrow redoxcline. In the revised MS we are more careful in discussing the halocline dynamics and clearly state that this is not supported by data, yet.

Referee: P. 6, line 20ff: "Due to increasing sulfide concentrations in water depths below the turbid layer and interaction of sulfide with the Ag/Cl pH electrode, a shift of pH of up to 0.2 pH units towards higher values was observed when comparing the pH logs of the way down with the pH logs of the way up (Fig. S1). This shift is dependent on the exposure time of the electrode and the respective sulfide concentrations and could not be quantified nor corrected for." May it be possible to quantify the effect in the laboratory by increasing the sulfide content of a test-solution?

Response: Please see the following response below.

Referee: P. 12, line 19ff.: "However, SI values calculated for the halocline suffer from the overestimated pH readings in the extremely sulfidic water of the halocline and are therefore not considered." This is a pity because supersaturation with respect to calcite within the halocline is the hypothesis presented to explain the growth of the Hells Bells. Thus, it would be really good to estimate the effect on the pH values (see above) and the resulting effect on SI. This information is essential for the validity of the presented hypothesis.

Response: Unfortunately, quantifying the pH shift is not possible because the sonde that we used was a rental sonde. However, we did this campaign again at El Zapote cenote in 2018 with the exact same type of sonde but a new one. The pH values were identical to the ones presented in the MS except for the values below the redoxcline which were significantly lower at its minimum values in around 42 m water depth (up to $\sim$0.25 pH units). We fully agree that this is essential for the validity of our hypothesis and therefore addressed this issue by including pH and SI calcite data from the sampling campaign in June 2018 into Supplement Fig. S2. We refer to this information in the method section and section "3.1.1 Calcite Saturation". This allows now to clearly show that calcite is oversaturated in the redoxcline and undersaturated in the halocline indicating calcite dissolution.

Referee: P. 13, line 5: ": : : from X to Y : : :" Is this an artefact from a previous version of the paper?

Response: Yes, thank you. It was corrected in the MS with the according values.

Referee: P. 13, line 5: Fig. 5 should be Fig. 4.

Response: Corrected as suggested.

Referee: P. 14, line 6: Figs 6 should be Figs. 5.

Response: Corrected as suggested.

Referee: P. 16, line 6ff.: Please state here that the samples were collected from "several" specimens. This information is important. In addition, it is (again) problematic that no dating is provided. Then, the data would not be related to the "presumably youngest part" of the bells, but the age of the samples could be precisely determined.

Response: Corrected as suggested. We are currently working on a Manuscript with the focus on age-dating of the Hells Bells.

Referee: P. 16, line 11: "soluble" should be "insoluble"?

Response: Yes, of course. Thank you. Corrected as suggested.

Referee: P. 16, line 21: d13Ccalcite values show a strong negative (not a positive) correlation with Sr/Ca and Ba/Ca if I correctly read Fig. 6.

Response: You are right. Corrected as suggested.

Referee: P. 16, line 25: In my opinion, the offset between the calculated and the measured d13C value of the HCO3 (2-5 permille) is substantial. Thus, speaking of "slightly lower" values is not correct.

Response: We agree and deleted "slightly", now saying that the s13C value of the measured HCO3 is lower than the calculated d13Ceq HCO3 vlaue.

Referee: Section 4: The introductory section could be deleted to make the paper more concise.

Response: We followed the referee′s suggestions and deleted this section.

Referee: Section 4.2: See above. The introductory section could be deleted to make the paper more concise.

Response: We followed the referee′s suggestions and deleted this section.

Referee: P. 22, line 7: Please provide a reference for reaction (R1).

Response: Reaction R1 was developed by the authors. However, in order to meet the referee′s comment we referenced to supporting literature that shows the process of anaerobic sulfide oxidation via nitrate ("...could be obtained with nitrate as terminal electron acceptor producing elemental sulfur and nitrogen under the consumption of protons (e.g. Bailey et al., 2009)."

Referee: P. 22, line 21: Please define "SD-OM".

Response: SD-OM is already defined in the MS above (". . .could be obtained with nitrate as terminal electron acceptor producing elemental sulfur and nitrogen under the

consumption of protons (e.g. Bailey et al., 2009)."

Referee: P. 22, line 27: "As organisms usually prefer to metabolize 12C (it takes less energy to break the 12C bond instead of 13C) they effectively consume HCO3- with lower d13C values, which subsequently results in higher d13CHCO3- values in the remaining dissolved inorganic carbon" It is true that the organisms preferentially metabolise 12CO2, but they do not "effectively consume HCO3- with lower d13C values". The preferential consume of 12CO2 (and the related increase in the d13C value of the CO2) leads to chemical and isotopic reactions resulting in conversion of HCO3 into CO2 and an increase in the d13C value of the HCO3 reservoir.

Response: We agree and deleted "effectively consume HCO3- with lower d13C values" . We changed the according sentence to "Organisms usually prefer to metabolize 12C (it takes less energy to break the 12C bond instead of 13C), which results in higher ïĄď13C-HCO3- values in the remaining dissolved inorganic carbon."

Referee: P. 23, line 2: "It was shown before that Hells Bells form within the freshwater indicated by d234Uinitial values of 16–25 ‰ of the Hells Bells calcite (Stinnesbeck et al., 2017b)." Please explain this statement. Why do these values suggest precipitation within freshwater? Due to the non-marine d234U value (lower than 150 permille)? Or has the d234U value of the water in the cenote been determined (at different depths)? Actually, freshwater often has higher d234U values than seawater

Response: We agree that we cannot state this without showing the d234U values over the depth range of the water body. We removed the argument of d234U and changed the sentence to "It was suspected before that Hells Bells form within the freshwater body of El Zapote cenote (Stinnesbeck et al., 2017b)."

Referee: P. 24, line 8: "Hells Bells formed in modern to historic times : : :" How do you know that? Is this statement based on the few U-series ages reported by Stinnesbeck et al. (2017b)? It may very well be possible that there are much older specimens in the same cenote.

Response: This statement is based on the U-series measurements and the 14C age of the tree stem which is covered by small specimen of Hells Bells. We agree that there should be much older specimen considering their enormous size. We changed the sentence to "Hells Bells formed in modern to at least historic times and occur…" by inserting "to at least historic times" in order to meet the referee's critique.

Referee: P. 24, line 13ff.: "Therefore, we propose that growth of Hells Bells is a non-permanent episodic process which majorly depends on a highly variable halocline elevation in the cenote (Fig 10)." See my major comment above. The probably very different growth rate of the bells and the seasonal to episodic dynamics of the depth of the halocline need to be discussed in detail.

Response: We fully agree and added a detailed discussion on growth rates to the revised MS. However, although we are convinced that the halocline dynamic is an interesting and upcoming research topic we believe that a detailed discussion on the dynamic elevation of the depth of the halocline is beyond the scope of the MS.

Referee: P. 24, line 16ff.: "Extraordinary recharge events (e.g. hurricanes) must have a significant effect on the depth position of this layer : : :" See above. Even if this is the case, it is not clear whether these episodic changes would be recorded by the slowly growing Hells Bells.

Response: The detailed discussion on growth rates in the revised MS demonstrates that short-term episodic events could be recorded in Hells Bells growth.

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