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Biogeosciences Discussions

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.

Anonymous Referee #2

Received and published: 26 February 2019

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 long-term 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 rate of the Hells Bells.

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.

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.

Detailed comments:

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).

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?

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.

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

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

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

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.

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

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.

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.

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

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

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

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

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.

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 . . .

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.

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.

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.

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