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Holocene sea-level rise evidenced in Hells Bells $^{234}\text{U}/^{238}\text{U}$ ratio and geochemical composition

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Abstract. Hells Bells are underwater secondary carbonates discovered in sinkholes (cenotes) southeast of Cancun on the north-eastern Yucatán Peninsula, Mexico. These authigenic calcite precipitates, reaching a length of up to 4 m, most likely grow in the pelagic redoxcline. Here, we report on detailed $^{230}\text{Th}/\text{U}$ -dating and in-depth geochemical and stable isotope analyses of specimens from cenotes El Zapote, Maravilla and Tortugas. Hells Bells developed during the end of MIS5b/c (~96–90 thousand years ago) and again since the early Holocene, with active growth until present day. The temporal evolution of the geochemistry and isotope composition of Hells Bells calcites appears closely linked to the mid to late Holocene sea-level rise, which reflects changing hydrological conditions of the aquifer. A stabilization of sea level combined with aquifer occlusion during the past ~8 thousand years probably led to a reduction in hydraulic conductivity and a desalinization of the freshwater layer as indicated by decreasing Sr/Ca values. In addition, initial ($^{234}\text{U}/^{238}\text{U}$) activity ratios ($\delta^{234}\text{U}_0$) in the Bells calcite decrease from 55 to 15‰ as sea level converges toward its present state. We propose that the Holocene sea-level rise drives desalinization and subsequent deceleration of leaching of excess ^{234}U from the previously unsaturated bedrock.

28 Introduction

29 Impressive bell-shaped speleothems hanging from cavern ceilings and walls were recently discovered in 30–40 m
30 water depth in a small cluster of meromictic sinkholes (e.g., cenote El Zapote) on the north-eastern Yucatán
31 Peninsula (YP) in Mexico (Fig. 1)¹. These up to 4 m long conically downward expanding calcareous structures
32 called Hells Bells were formed underwater¹. Recently, Hells Bells formation was suggested to initially result from
33 CO₂-degassing of ascending gas bubbles that accumulate at cave irregularities and further growth of these
34 structures in the carbonate-saturated freshwater layer of cenote El Zapote². Alternatively, Ritter et al³ proposed
35 that the actual growth of Hells Bells is most likely restricted to the pelagic redoxcline, a 1–2 m thick zone of steep
36 redox-gradients of electron acceptors and reduced chemical species above a sulfidic halocline. The redoxcline
37 overlaps with a distinct milky white horizontal cloud, the turbid layer, into which some Hells Bells partly reach or
38 completely hang inside. Based on hydrogeochemical profiles, a biologically induced authigenic calcite precipitation
39 within the turbid layer was hypothesized^{1,3}. In any case, the growth of these speleothems is most likely not
40 continuous. Instead, the corroded lobes of dog-tooth spar crystals and microcrystalline calcite layers of Hells Bells
41 may represent alternating phases of growth and intermittent dissolution, which suggest an episodic elevation of the
42 halocline and, thus, the redoxcline and zone of calcite precipitation^{1,3}. So far, the timing of Hells Bells growth
43 remained uncertain since only two small specimens have been ²³⁰Th/U-dated yielding ages between 5,200 and
44 300 years^{1,2}. To better constrain the timing and growth rate of Hells Bells, we conducted a systematic study using
45 ²³⁰Th/U-dating on several large specimens. In addition, small nodules growing on a drowned tree trunk infer active
46 growth within the redoxcline. Moreover, we have investigated the geochemical composition of these Bells and
47 discovered a small but systematic temporal trend in initial (²³⁴U/²³⁸U) activity ratios and the Bells Sr/Ca ratios that
48 seems closely linked to the terminal sea-level rise of the mid to late Holocene. (²³⁴U/²³⁸U) activity ratios are reported
49 here in delta notation ($\delta^{234}\text{U}$ values), representing the deviation of (²³⁴U/²³⁸U) from secular equilibrium ($\delta^{234}\text{U} =$
50 (²³⁴U/²³⁸U)-1). The initial value of $\delta^{234}\text{U}$ ($\delta^{234}\text{U}_0$) can be calculated from the measured $\delta^{234}\text{U}_m$ by correcting it for the
51 decay of excess ²³⁴U since the time of sample formation (t):

$$\delta^{234}\text{U}_0 = \delta^{234}\text{U}_m * e^{\lambda_{234} * t}$$

53 ²³⁴U and ²³⁸U as well as Sr and Ca enter freshwater and seawater from host rock dissolution with preferentially
54 leaching of ²³⁴U due to the processes of alpha-recoil. In general the Sr/Ca ratios and $\delta^{234}\text{U}_0$ values are suspected
55 constant for seawater while in cave drip waters and speleothems, Sr/Ca ratios may depend on the amount of
56 precipitation and other processes⁴⁻⁶. The $\delta^{234}\text{U}_0$ value is influenced by several processes, such as the alpha-recoil
57 process, host rock dissolution, and redox-behavior of Uranium⁷⁻¹⁰. In general, the $\delta^{234}\text{U}_0$ value of secondary

58 carbonates from the northern YP is close to secular equilibrium¹¹⁻¹³ and hence lower than the $\delta^{234}\text{U}_0$ value of
59 seawater ($146.8 \pm 0.1\%$ ¹⁴). In a recent study from southwest Nevada, it was suggested that even under dry
60 conditions (e.g., during periods of a low water table), alpha-recoil causes excess ^{234}U to accumulate in damaged
61 crystal lattice sites and/or on fractured surfaces of the bedrock and sediments, which may then be 'captured' as
62 the water table returns¹⁵. While ground-waters in general reveal changes of $\delta^{234}\text{U}_0$ values of several hundred ‰
63 through time, Hells Bells show only very small changes of $<40\%$ during the last ~8 ky.
64 The YP represents an extended limestone platform of horizontally layered carbonate rocks of Cretaceous to
65 Pleistocene ages^{16,17}. The Yucatán Karst Aquifer (YKA) hosts the largest known network of underwater caves in
66 the world^{16,18}. Climate driven sea-level fall and rise by $>100\text{ m}$ ¹⁹ caused large parts of the cave system to fall dry
67 and submerge, respectively^{11,18,20,21}. Modern water levels were reached around 4.5–3.8 ky ago^{20,22,23}. The water
68 level of the cenotes in the north-eastern YP is known to be roughly equal to sea level due to connective passages
69 with the Caribbean Ocean and the low hydraulic gradient of about $1\text{--}10\text{ cm km}^{-1}$ ²⁴. Precipitation rapidly infiltrates
70 through the porous limestone into the underlying coastal aquifer consisting of a meteoric water mass, the freshwater
71 lens, above saline water intruding from the coast²⁵. The thickness of the freshwater lens varies between $<10\text{--}100$
72 m and is generally thinner towards the coast²⁶, resulting in a higher salinity of the freshwater lens close to the coast
73 than in inland areas²⁵. The halocline separates the meteoric and marine water bodies and is usually characterized
74 by undersaturation with respect to CaCO_3 , leading to cave formation and conduit enlargement in the coastal
75 carbonate aquifer^{18,27-29}.

76
77 **Figure 1: The study area and schematic cross-sections of the investigated cenotes (a) Map of the study area with**
78 **respect to the Yucatán Peninsula and Mexico. (b-d) Cross-section of the cenotes El Zapote, Tortugas and Maravilla**
79 **showing the host rock and the sedimentary deposits, such as debris, and Hells Bells speleothems. The grey shaded**

80 area at the freshwater-halocline interface refers to the redoxcline, where modern carbonate precipitation is suspected
81 according to Ritter et al³ and Stinnesbeck et al¹.

82 Results

83 Hydrogeochemistry of cenote El Zapote

84 Uranium concentrations are nearly constant at $\sim 12 \text{ nmol L}^{-1}$ in the upper 35 m of the oxygenated freshwater layer
85 and instantly drop by an order of magnitude as soon as the water becomes anoxic (Supplementary Fig. 1b). $\delta^{234}\text{U}$
86 values are nearly constant throughout the freshwater layer with values of $16 \pm 1\text{‰}$ and increase within the halocline
87 to significantly higher values of $60 \pm 3\text{‰}$ at 45 m water depth. Uranium concentrations are anticorrelated with $\delta^{234}\text{U}$
88 values ($r_{\text{U}/\delta^{234}\text{U}} = -0.68$).

89 $^{230}\text{Th}/\text{U}$ -ages and $\delta^{234}\text{U}_0$ values

90 $^{230}\text{Th}/\text{U}$ -dating of Hells Bells samples yielded a large spread of U concentrations ranging by a factor of 15 from
91 209.893 ± 0.016 to $3100 \pm 20 \text{ ng/g}$. ^{232}Th concentrations are variable ranging from 0.16242 ± 0.00040 to $5.795 \pm$
92 0.015 ng/g (Supplementary Table 1). The measured $\delta^{234}\text{U}$ values vary from 15.1 ± 1.2 to $59.9 \pm 4.4\text{‰}$, and the
93 $^{230}\text{Th}/\text{U}$ ages range from recent to as old as 96 ky. To estimate the potential influence of initial (either detrital or
94 freshwater derived) excess $^{230}\text{Th}_{\text{xs}}$ on the $^{230}\text{Th}/\text{U}$ age, a first order correction was applied. Here, we assume one
95 single source of contamination with a moderately elevated detrital ($^{230}\text{Th}/^{232}\text{Th}$) activity ratio of 2 ± 1 , which is based
96 on previous observations from speleothems of cave sites on the YP and the Caribbean realm^{11,12,30-34}. When using
97 this correction model, the corrected ages for the measured Hells Bells samples range from $95.81 \pm 0.52 \text{ ky}$ to
98 modern. Initial $\delta^{234}\text{U}_0$ values vary from 15.1 ± 1.2 to $62.6 \pm 4.6\text{‰}$, with the highest values observed in the early
99 Holocene and systematically decreasing values for the mid- to late Holocene (Supplementary Table 1). In fact,
100 $\delta^{234}\text{U}_0$ values steadily decline in all studied Bells from three different cenotes from 55‰ to around 20‰ between
101 $\sim 8\text{--}4 \text{ ky}$, followed by a minor decrease to values of $\sim 15\text{‰}$ to present (Fig. 2). $\delta^{234}\text{U}_0$ values from MIS5b/c ($\sim 96\text{--}90$
102 ky ago) are intermediate with $30\text{--}35\text{‰}$. Overall, $\delta^{234}\text{U}_0$ values from various Bells and cenotes thus reveal an
103 identical temporal variability, which must reflect the isotopic composition of the water in which those carbonates
104 have formed, since there is no fractionation during the incorporation of uranium into carbonates³⁵.

Figure 2: $\delta^{234}\text{U}_0$ values versus age. Note the broken axis (10–90 ky BP) for absolute ages. Uncertainties are given as 2σ margins.

As expected, the root of Big Bell reveals the oldest growth phase dating back to 95.81 ± 0.52 ky (Fig. 2 and Supplementary Fig. 2b). Big Bell and ZPT-7 yield ages spanning from the last glacial-interglacial termination to present. The growth of ZPT-7 starts on top of the marine limestone slab (host rock) (Fig. 3; Supplementary Fig. 2c and 3). The determined ages are mostly in stratigraphic order. Layers within ~ 3.5 cm distance from the marine limestone slab, yielded ages between 15.5 and 10 ky (Fig. 3, Supplementary Fig. 2c and 3). One of these samples was taken immediately adjacent to a growth interruption, which is macroscopically identified as a black rim conformed by pyrite (Supplementary Fig. 2c). This sample yielded a significantly older age (15.51 ± 0.21 ky) than the two samples above, thus representing a major stratigraphic inversion. A similar age of 15.02 ± 0.13 ky was obtained from a sample of the root of Big Bell, which was also sampled near a thin layer of pyrite (Supplementary Fig. 2b). Since we do not know whether the pyrite layer – or the processes that led to its formation – may have had an influence on the geochemistry of the adjacent calcite layers and thus the $^{230}\text{Th}/\text{U}$ ages, or whether this strong

120 inversion is the result of a mixture of Hells Bells material of different ages, we exclude these older samples from
 121 the following discussion and focus on the mid- to late Holocene samples. From 7.7–2.5 ky, i.e., from 3.7–53.5 cm,
 122 the ages of ZPT-7 suggest more regular growth with an average growth rate of about $100 \mu\text{m yr}^{-1}$ (Fig. 3). At 2.5
 123 ky (53.5 cm), a growth interruption is evident with a duration of about 1 ky (Fig. 3, Supplementary Fig. 3). The tip
 124 of ZPT-7 at 56.7 cm is dated to an age of 1.284 ± 0.083 ky, which possibly corresponds to the timing of Bell
 125 downfall. $^{230}\text{Th}/\text{U}$ -dating of the antapical ends of Tree Bells collected from different water depths yielded ages
 126 between 0.18 ± 0.13 and 0.01 ± 0.15 ky. Moderate uranium concentrations together with high detrital ^{232}Th and a
 127 low ($^{230}\text{Th}/^{232}\text{Th}$) activity ratio result in large age uncertainties of these samples, which, however, are most likely
 128 modern.

129
 130 **Figure 3: Ages and geochemistry of ZPT-7 along the growth axis. Apical root ends up with carbonate host rock (star**
 131 **symbol). Sample spots are indicated by blackened areas in the image on the left. Major growth discontinuities are**
 132 **highlighted by grey bars. Note the increasing trends of $\delta^{18}\text{O}$ values and molar S/Ca ratios as well as the decreasing**
 133 **trends of Sr/Ca ratios and $\delta^{13}\text{C}$ values. The ages and geochemical results can be found in Supplementary Table 1**
 134 **and 2. dfa = distance from the apex.**

135 **Geochemistry of Hells Bells**

136 The host rock carbonate shows stable carbon and oxygen isotope values ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values) of -4.85‰ and -3.75‰ , respectively. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the Hells Bells samples are ranging from -11.07 to -14.32‰ and from -6.39 to -4.34‰ , respectively. Hence, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of Hells Bells are different from those of
139 the host rock. Most samples form a distinct cluster in the stable isotope plot (Fig. 4a), which correspond to the mid-
140 to late Holocene samples. Here, $\delta^{13}\text{C}$ values correlate inversely with $\delta^{18}\text{O}$ values ($r_{\delta^{13}\text{C}/\delta^{18}\text{O}} = -0.46$, slope = -0.85).
141 There are only a few samples from cenote Tortugas that deviate from this trend, as they exhibit slightly less negative
142 $\delta^{13}\text{C}$ values (-11.36‰ on average) than the other samples (-13.06‰ on average). The two oldest samples (~ 96
143 and 90 ky) also plot closely to this cluster and only slightly differ from the rest by showing the most negative $\delta^{18}\text{O}$
144 values (-6.39‰ and -6.10‰). The trend in the isotope correlation is also visible through time, with decreasing $\delta^{13}\text{C}$
145 values and increasing $\delta^{18}\text{O}$ values towards younger ages (Fig. 3 and 4).

146
147 **Figure 4: Geochemistry of all analyzed Hells Bells samples. The different symbols represent the different cenotes.**
148 **Samples <8.5 ky BP are colour-coded depending on their respective age. (a) Stable carbon isotope values ($\delta^{13}\text{C}$)**
149 **plotted against stable oxygen isotope values ($\delta^{18}\text{O}$) of all analyzed Hells Bells samples, and the host rock**
150 **from the root of ZPT-7 (El Zapote cenote). (b) Sr/Ca against Ba/Ca ratios of all analyzed Hells Bells samples and the**
151 **host rock sample. Sr and Ba contents of Hells Bells calcite are linearly correlated and indicate that the initial Sr/Ba**
152 **ratio of the host rock is preserved in Hells Bells carbonates. The geochemical results can be found in Supplementary**
153 **Table 2.**

154 Hells Bells carbonates show strongly correlated Sr/Ca and Ba/Ca ratios, and the linear fit intersects with the Sr/Ca
155 and Ba/Ca ratio of the host rock (Fig. 4b). The ratios of these samples show a decreasing trend with increasing
156 distance from the apex and decreasing age, respectively (Fig. 4b). As for the stable isotopes, the Sr/Ca and Ba/Ca
157 ratio of the oldest samples (96–90 ky) show slightly different values than the general trend.
158 Dark, brown-colored layers identified on the polished half of ZPT-7 correspond to elevated Mn/Ca and Fe/Ca values
159 (Fig. 3) and show a large scatter. The molar ratio of Mg/Ca ($24\text{--}40 \times 10^{-3}$) appears rather constant through time
160 (Fig. 3). In contrast to the metal/calcium ratios, the multivalent non-metal Sulphur (S) reveals an opposing trend
161 with an increasing S/Ca ratio of ZPT-7 from ~ 0.1 to 2.7×10^{-3} with decreasing age (Fig. 3). These geochemical
162 trends are thus evident throughout all studied Hells Bells, and even in the nearby cenotes Maravilla and Tortugas
163 (Fig. 4).

164 **Discussion**

165 **$^{230}\text{Th}/\text{U}$ -chronology and sea level**

166 Radiometric dating traces the age of carbonate precipitation, and in accordance with relative sea-level elevation
167 during MIS-5b/c and the Holocene, two phases of Hells Bells growth are identified (Fig. 5): (1) From $\sim 96\text{--}90$ ky,
168 i.e., during MIS-5b/c, as indicated by two ages from the root of Big Bell. (2) The Middle to Late Holocene, more
169 specifically most of the last 8.5 ky, where the $^{230}\text{Th}/\text{U}$ -dating results obtained here provide clear evidence for partly
170 continuous growth of Hells Bells, for example from 7–2.5 ky in ZPT-7, with minor age inversions.

172 **Fig. 5: $^{230}\text{Th}/\text{U}$ ages of Hells Bells samples collected between 29 and 37 m water depth within the cenotes plotted**
173 **versus relative sea level from the stack of Spratt and Lisiecki³⁶. The original position of Hells Bells samples collected**
174 **from the floor of cenote El Zapote (black symbols) was estimated to be 33 ± 5 m water depth based on the present-day**
175 **occurrence of Hells Bells in water depths between 28 and 38 m. Due to the subaqueous nature of Hells Bells, the**
176 **water table and hence sea level, must be at the depth level of the Bells, or above (grey shaded area). Marine isotope**
177 **substages (MIS) proposed by Railsback et al³⁷ are shown at the bottom.**

178

179 The two ages of ~ 96 and 90 ky obtained from the root of Big Bell reveal that Hells Bells formation is not a
180 phenomenon restricted only to the Holocene, but instead already existed at least since MIS-5b/c (Fig. 5). The
181 extensive hiatus between phase (1) and (2) advocates for a sea-level control on carbonate formation. In times
182 when global sea level was between -38 and -130 m (Fig. 5)³⁶, growth of Hells Bells was inhibited, and the exposed
183 carbonate was potentially subject to subaerial weathering, i.e., Bell dissolution or secondary carbonate precipitation
184 from meteoric waters. Thus, pieces of initial Big Bell growth outlasted the aerial exposure during the sea-level low-
185 stand of the last glacial for tens of thousands of years until sea level rose again and growth of Hells Bells re-
186 initiated. The $^{230}\text{Th}/\text{U}$ -dating results of ZPT-7 further show that Hells Bells calcite can be dated at century scale
187 resolution. Minor age inversions identified throughout the specimen are likely due to the complex and yet unknown
188 internal structure of Hells Bells and most likely result from deviations from the growth axis during sample collection.
189 The mid- to late Holocene timing of Hells Bells growth confirms previous punctuated observations^{1,2}. Between 7.7
190 and 2.5 ky (3.7 – 53.4 cm), $^{230}\text{Th}/\text{U}$ -ages of ZPT-7 show an average growth rate of about $100\text{ }\mu\text{m yr}^{-1}$ (Fig. 3 and
191 Supplementary Fig. 3). These Hells Bells growth rates are in the same order of magnitude as those calculated from
192 $^{230}\text{Th}/\text{U}$ -dating by Stinnesbeck et al¹ and two orders of magnitude higher than other types of subaqueous
193 speleothems, like mammillary calcite or folia^{38–40}. The hand-sized Hells Bells speleothem TL4 from El Zapote and
194 the ones from Maravilla and Tortugas show lower growth rates (~ 4 – $18\text{ }\mu\text{m a}^{-1}$) than ZPT-7 ($\sim 100\text{ }\mu\text{m a}^{-1}$). One
195 explanation for that might be that those Bells may have experienced continuous changes between growth and
196 dissolution of calcite, resulting in lower net growth since these Bells were hanging in greater depths, i.e., closer to
197 the acidic water below the redoxcline. This assumption is supported by the strong lamination of these samples
198 (Supplementary Fig. 4). The ages of 2.8 and 1.3 ky, determined for the lowermost parts of Big Bell and ZPT-7,
199 respectively, may refer to the times when these specimens broke off the cave ceiling and fell on the cave floor,
200 where they stopped growing. Whether these break-offs were gravitationally triggered by the weight of the Bells or
201 even by a devastating event (e.g., earthquake) remains speculative. Interestingly, the age of 1.3 ky coincides with
202 a suspected age of seismic activity on the coast of Quintana Roo and the occurrence of a tsunami deposit⁴¹.
203 Verification of recent growth of Hells Bells is challenging considering the low growth rates and the partly high
204 concentrations of ^{232}Th (up to 6 ng/g) in Tree Bell samples. Nevertheless, the 2 – 3 mm thick samples collected from

205 water depths between 32.7 and 37.3 m yield very young ages of a few decades to centuries (Supplementary Fig.
206 2a). Thus, we suggest the growth of Hells Bells to be presently active and that the elevation of the halocline, and
207 thus, the zone of Hells Bells growth, varied on the scale of several meters within this period (few decades to
208 centuries).

209 Overall, the results of the $^{230}\text{Th}/\text{U}$ -dating on different Hells Bells specimens from different cenotes on the YP thus
210 reveals two phases of Hells Bells growth. Phase 1 around 96–90 ky and semi-continuous growth of Hells Bells
211 since about 8.5 ky until present (phase 2).

212 **Stable carbon and oxygen isotopes**

213 The stable carbon isotope record measured in Hells Bells calcite differs distinctively from values determined in the
214 host rock (Fig. 4a). Hells Bells calcite samples of 96–90 ky show $\delta^{13}\text{C}$ -values around -8‰ , while Holocene samples
215 reveal values ranging from -13‰ in cenote Zapote to -11‰ in cenote Tortugas. The dissolved CO_2 in the
216 redoxcline is fueled by organic matter decomposition in the anoxic saltwater layer and host rock dissolution
217 buffering the acid produced in microbial organic matter decay via sulphate reduction³. Consequently, changes in
218 $\delta^{13}\text{C}$ values could reflect a change in vegetation type (C_3/C_4 plants), a change in vegetation density (pCO_2 of the
219 soil), a change in carbon source (organic matter vs. host rock), or a combination of all of them.

220 The stable oxygen isotope record measured in Hells Bells calcite mainly depends on the isotopic composition of
221 the freshwater layer, which in turn depends on the isotopic composition of precipitation since groundwater on the
222 YP is a long-term integrator of precipitation and infiltration⁴². There are several studies that have obtained modern
223 $\delta^{18}\text{O}$ values from cenotes with values for groundwater between -2 and -5‰ ⁴²⁻⁴⁵. Long-term monitoring of drip- and
224 groundwater in the Rio Secreto Cave near Playa del Carmen about 30 km south of our study area (e.g., El Zapote)
225 on the northeast of the YP, showed that the $\delta^{18}\text{O}$ values of groundwater are consistent with the annual amount-
226 weighted $\delta^{18}\text{O}$ value of rainfall, while its temporal isotopic stability suggests that it integrates several years of
227 rainfall⁴⁵. In the tropical Atlantic region, $\delta^{18}\text{O}$ values of precipitation are generally linked to summer rainfall amount,
228 a relationship which is based on the type and source of wet season (convective) versus drier season (orographic)
229 rainfall⁴⁶⁻⁴⁸. Convective rainfall during the wet summer season associated with frequently occurring tropical storms
230 and hurricanes shows characteristic depleted isotopic values⁴⁸. A study in the northwestern part of the YP showed
231 that the depleted isotopic composition associated with a single hurricane event can disturb the baseline $\delta^{18}\text{O}$ value
232 of groundwater for a few years⁴⁹. Based on these findings, changes in $\delta^{18}\text{O}$ values of Hells Bells calcite may
233 represent long-term changes of local precipitation amount and/or convective activity. The temporal evolution of
234 $\delta^{18}\text{O}$ values in the ZPT-7 speleothem are lowest around 7 ky, i.e., the mid-Holocene, and then slightly increase
235 towards modern times. The observation of highest precipitation amounts and/or convective intensity during the

236 mid-Holocene and a minor drying trend over the past ~7 ky agrees well with stalagmite records from Guatemala⁵⁰
237 and Mexico⁵¹.

238 **Geochemistry and sea level**

239 Due to the low hydraulic gradient (1–10 cm km⁻¹) of the YKA, the water level within caves and cenotes on the north-
240 eastern YP is known to be roughly equal to sea level, especially in areas close (few kilometers distance) to the
241 coast²⁴. Hells Bells occur in a narrow depth interval of about 13 m from –25 to –38 m water depth. Ritter et al³
242 proposed that the actual growth of Hells Bells is most likely restricted to the 1–2 m thick pelagic redoxcline above
243 a sulfidic halocline. They also suggested an episodic elevation of the halocline and, thus, the redoxcline and zone
244 of calcite precipitation. Hence, the calcite formation reflects the chemical steady state between upward element
245 fluxes, host rock dissolution, and removal of elements from carbonate precipitation and horizontal freshwater flow
246 to the ocean. Under these premises, Hells Bells formation places constraints on the minimum height of the
247 redoxcline and halocline (reflecting the competition of sea level and freshwater layer thickness). This is opposite to
248 the water level constraints obtained from submerged speleothems, which grow in dry caves and therefore provide
249 an upper limit for past water level elevation (sea level)^{11,52}.

250 Geochemical changes of the Bells are well documented in the ratios of Sr/Ca and Ba/Ca, and values of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$
251 and $\delta^{234}\text{U}$, which all systematically change throughout the last ~8 ky. While the processes driving the geochemical
252 evolution of the Hell Bells calcite are considered highly complex³, the continuous change of, for example, $\delta^{234}\text{U}$
253 values through time is unique. The large spatial scale of systematic geochemical changes of the water interface
254 and calcite chemistry is well attested by Hells Bells samples from the cenotes El Zapote, Maravilla and Tortugas,
255 which show consistently decreasing Sr/Ca ratios and thus a decrease in the salinity of the freshwater aquifer during
256 the last ~8 ky (Fig. 6b). Sr/Ca and Cl/Ca ratios of calcite raft deposits in cenotes Ich Balam and Hoyo Negro about
257 80 km south of the Hells Bells cenotes show similar changes in the salinity of the freshwater aquifer with a relatively
258 high salinity during the mid-Holocene (~8.3–7.8 cal ky BP), followed by a continuous decline in salinity over the
259 past ~7 ky²⁵. Calcite rafts form at the air-water interface in CaCO₃ saturated waters through CO₂ degassing and
260 evaporation. They form conically shaped piles as they sink and accumulate on the cave bottom, thereby providing
261 records of the upper part of the freshwater aquifer⁵³. On the scale of days to weeks, instrumental monitoring has
262 shown that heavy rainfall events (i.e., hurricanes) can cause turbulent mixing between the marine and the meteoric
263 waters, leading to an increased freshwater salinity^{54–56}. Thus, the authors suggest that the decline in aquifer salinity
264 during the last ~7 ky likely reflects a change in hydrology (drying trend) associated with a decreased freshwater
265 flow in the aquifer²⁵. Similarly, benthic microfossils from cenote Aktun Ha, 75 km south of the Hells Bells cenotes,
266 indicate a gradual decrease in freshwater salinity over the past ~4.3 cal ky BP²⁰. They found convincing

relationships between changing aquifer salinity and late Holocene precipitation patterns. However, the authors also point out that other factors may influence the salinity of the aquifer, such as aquifer occlusion and coastal sedimentation, both long-term processes resulting from sea-level stabilization, which may gradually reduce hydraulic conductivity and turbulent mixing of the aquifer, leading to a desalinization of the freshwater layer²⁰. Reconstructions of middle to late Holocene sea-level rise on the YP (Fig. 6a)²³, represented by a 3rd order polynomial fit of sea-level index points from Mexico and Belize, match extraordinarily well with the pattern of Sr/Ca ratios of Hells Bells with an average deviation of 8% from the sea-level fit (Fig. 6b). These reconstructions are based on archives, such as mangrove peat, corals and microbial mats²³, and encompass an area from 16.3–20.5°N, 86.5–92.1°W. Given the clear relationship between a long-term desalinization of the freshwater aquifer and sea-level stabilization, we suggest that on millennial time-scales, sea level acted as the major driver for mid- to late Holocene changes in aquifer hydrogeochemistry on the YP and that drying trends, as suggested by Kovacs et al²⁵, rather act on shorter (decadal-centennial) time-scales. This hypothesis gains even more support when looking at temporal changes in (²³⁴U/²³⁸U) activity ratios of the aquifer.

The pattern of $\delta^{234}\text{U}_0$ values matches the progression of middle to late Holocene sea-level rise on the YP even better than that of Sr/Ca ratios, presenting an average deviation of only 6% from the sea-level fit (Fig. 6). Over the past ~8 ky, $\delta^{234}\text{U}_0$ values decrease continuously from values around 55–60‰ to values between 15–20‰ as sea level converges toward its present state, roughly equivalent to an 8–10 m sea-level increase (Fig. 6c). $\delta^{234}\text{U}_0$ values of Hells Bells calcite reflect the (²³⁴U/²³⁸U) activity ratios of the paleo water in which they were formed. There might be several mechanisms involved in controlling $\delta^{234}\text{U}$ values of the aquifer. Highly ²³⁴U enriched U might be delivered from alpha recoil processes and U leaching, or can be supplied by ²³⁴U deficient U from dissolution of previously leached host rocks⁵⁷. Hence the origin and variability of freshwater $\delta^{234}\text{U}$ values and U concentration is complex. Changes in the geochemical environment of the water rock interaction can modify the $\delta^{234}\text{U}$ values and U concentrations. Changes in groundwater residence time can lead to uptake of more or less excess ²³⁴U. Accumulation of excess ²³⁴U in unsaturated soil or unleached bedrock can cause fluctuations of $\delta^{234}\text{U}$ values related to fluctuations of the water table¹⁵. Here, isotopic variations are very systematic and occur over large spatial scales. Isotopically enriched U is supplied through diffusion by the underlying saltwater, even if the concentration of uranium in the saltwater body is reduced due to anoxic conditions in which U behaves particle reactive. In contrast, the overlying freshwater seems rather homogeneous and is close to secular equilibrium (~16‰, Supplementary Fig. 1).

In a recent study, Wendt et al¹⁵ interpreted $\delta^{234}\text{U}_0$ values of subaqueous calcite from Devils Hole 2 cave as a proxy for water-rock interactions in the regional aquifer. They propose that changes in the elevation of the water table are responsible for changes in the amount of leached excess ²³⁴U from the bedrock and that variations in (²³⁴U/²³⁸U)

299 activity ratios therefore coincide with interglacial-glacial cycles. Although the setting of the YKA is distinctly different
300 from that of the Devils Hole in southwest Nevada, they both are subject to recurrent changes in water level elevation
301 on interglacial–glacial timescales. In Nevada, water table fluctuations are driven by variations in recharge amount
302 to the local groundwater flow system⁵⁸, whereas on the YP, they are associated with glacio-eustatic changes in
303 sea level¹⁸. Similarly to the findings of Wendt et al¹⁵, we suggest that the inundation of previously unsaturated
304 bedrock causes a concomitant change in $\delta^{234}\text{U}$ values of the groundwater with sea level and hence water table
305 rise as indicated by $\delta^{234}\text{U}_0$ values of Hells Bells calcite. While we cannot provide unequivocal proof of this
306 hypothesis, the systematic correlation of $\delta^{234}\text{U}$ values with sea level is outstanding and suggests that the evolution
307 of $\delta^{234}\text{U}$ values could be used as a regional proxy for the changes in relative sea-level.

308

309 **Figure 6: Hells Bells geochemistry and sea-level reconstruction during the past 8 ky. (a) Sea level index points from**
 310 **Belize and Mexico²³. The dashed blue curve is a 3rd order polynomial fit through all data points (b-e) Geochemistry**
 311 **(Sr/Ca ratio, $\delta^{234}\text{U}_0$ -, $\delta^{13}\text{C}$ -, $\delta^{18}\text{O}$ -values) of Hells Bells from cenotes El Zapote, Maravilla and Tortugas during the past**

312 ~8 ky. The very few Hells Bells data available so far from Stinnesbeck et al¹ and López-Martínez et al² are also shown.
313 The fitted sea-level curve (dashed blue line) is also plotted next to the Hells Bells geochemistry to allow for a more
314 direct comparison to the individual geochemical parameter. Uncertainties are given as 2σ margins.

315 Conclusions

316 Data obtained from ²³⁰Th/U-dating, geochemical and stable isotope analyses of several Hells Bells specimens from
317 the cenotes El Zapote, Maravilla and Tortugas on the north-eastern Yucatán Peninsula show that geochemical
318 records of subaqueous grown Hells Bells speleothems can be used as a proxy for paleo-hydrological conditions of
319 the local aquifer. The oldest ages (96–90 ky BP) even reach back to MIS5b/c and thus indicate that Hells Bells
320 outlasted aerial exposure during sea-level low-stands of the last glacial period and future the potential to identify
321 earlier phases of growth. ²³⁰Th/U-dating of the lowermost parts of Hells Bells and thus their youngest endings
322 suggest that growth reaches to modern times and is an ongoing process. Geochemical (Sr/Ca ratios) and isotopic
323 trends of δ²³⁴U₀ values of Hells Bells calcites over the past ~8 ky follow the gradual increase and stabilization of
324 sea level well. We suggest that a stabilization of sea level towards the late Holocene probably led to a desalinization
325 of the freshwater layer as indicated by decreasing Sr/Ca ratios. This is the first study to show that decreasing δ²³⁴U₀
326 values of Hells Bells coincide with the final Holocene sea-level rise in the Caribbean. We propose that with the
327 deceleration of Holocene sea-level rise towards its present state, the contribution of accumulated excess ²³⁴U to
328 the aquifer decreased equally, and thus causes this unique empirical relationship. If future studies confirm this
329 observation, the δ²³⁴U values of Hells Bells calcites could be used as a regional proxy for sea-level reconstruction
330 in that region.

331 Methods

332 Hells Bells samples

333 The three studied cenotes (El Zapote, Tortugas and Maravilla) are located southwest of Cancún, in the Mexican
334 federal state of Quintana Roo (Fig. 1). Cenote El Zapote (20°51'27.78"N 87°07'35.93"W) is water-filled and
335 connected to the surface by a 28 m deep vertical shaft (Fig. 1a). The freshwater lens and the saline water mass
336 are separated by a thick halocline reaching from 36.7–51.7 m water depth (Fig. 1a)⁵⁹. At 28 m depth below the
337 water level, the cave walls diverge almost horizontally and form a 60 to >100 m wide cavern, reaching to a depth
338 of 54 m¹. A 20 m high debris mound in the center of the cave is built up by limestone blocks and smaller debris,
339 large stems of jungle trees and other vegetation falling in from the surface as well as abundant organic matter¹.
340 Hells Bells hanging from the cavern ceiling and walls and reaching lengths of up to >4 m appear in water depths of

341 28–38 m (Fig. 1a)¹. Cenote Tortugas (20°51'11.7"N 87°06'30.1"W) is located 24 km west of Puerto Morelos coast
342 and about 2 km east of cenote El Zapote. The cenote shows a large circular opening of about 25 m diameter and
343 is slightly asymmetric in cross-section (Fig. 1b). A debris mound lies against the wall of one side of the cenote and
344 dips towards the opposite side from 25 to around 60 m water depth. Here, Hells Bells appear in water depths from
345 25–35 m¹. Cenote Maravilla is located about 16 km west of the coast of Puerto Morelos (20°52'18.9"N
346 87°01'24.5"W). The cenote is bottle-shaped in cross section with a central debris mound (Fig. 1c). Hells Bells
347 appear in water depths from ~19 to at least 32 m. The selected Hells Bells are composed of horizontally laminated
348 calcite layers, with the lowermost (youngest) parts of the Bells frequently ending into mm to cm sized, elongated
349 dog-tooth calcite crystals^{1,3}.

350 Here we study three different types of Hells Bells samples from cenote El Zapote. (1) The root and bottom of a 1.8
351 m long Hells Bells specimen termed Big Bell. This specimen was recovered from the cenote floor in 2017 and is
352 presently displayed at the visitor center of El Zapote Eco Park. A slice of the uppermost root was cut with a diamond
353 saw and was polished subsequently. Samples were drilled perpendicularly to the presumed growth axis with a
354 Dremel tool using a diamond coated stainless-steel drill. Samples from the bottom of Big Bell were manually
355 removed and homogenized by grinding in an agate mortar. (2) An elongated ~60 cm long Hells Bells specimen
356 called ZPT-7¹ was – as the Big Bell – collected from the floor of cenote El Zapote. It was vertically cut in half, thin
357 sections were prepared from one half, and the other half was polished. ZPT-7 samples were drilled along the
358 presumed growth axes and along visual growth layers of about 0.5–1 mm thickness. (3) Some smaller Hells Bells
359 of 5–8 cm size (Tree Bells) growing over a range of ~5 m water depth on a tree trunk that has fallen into the cenote.
360 These carbonates were collected in June 2017 from seven water depth levels between 31.3 and 37.3 m. Their
361 geochemical composition (trace elements and stable isotopes) was previously published by Ritter et al.³. To obtain
362 the youngest parts of individual Hells Bells, the samples were microscopically studied, and only samples with
363 apparently fresh, well-accentuated crystal tips were chosen for further analyses. The sampling of the small Tree
364 Bell fragments differs from the others since the sample material for ²³⁰Th/U-dating was not taken as aliquots from
365 a homogeneous powder used for geochemical analysis. Here, sample material for dating was taken close to the
366 areas where sample material for geochemical analysis was collected. In 2018, additional small Hells Bells were
367 collected in cenote El Zapote (TL4), but also from the nearby cenotes Maravilla (MIII) and Tortugas (T7 and T12).
368 They were vertically cut, samples for geochemical analyses were drilled, and thin sections prepared. In the
369 following, all depth information on Hells Bells samples refers to the distance from the apex. Aliquots of all samples
370 were taken for the subsequent geochemical analyses. In addition to carbonate samples, water at cenote El Zapote
371 was sampled in 2018. Water samples between 0–36 m were retrieved using a 0.5 m high Polyethylene FreeFlow
372 bottle (HYDRO-BIOS, Kiel, Germany), and samples between 36–52 m were collected by technical divers by

373 drawing up the water of the desired sampling depth into 140 ml sterile PE-luer-lock syringes with an attached three-
374 way valve.

375 ²³⁰Th/U-dating

376 In total, 73 ²³⁰Th/U ages of Hells Bells samples were analyzed by MC-ICP-MS (Thermo Fisher Neptune^{plus}) at the
377 Universities of Heidelberg and Mainz. The applied sample treatment, mass spectrometry and data treatment are
378 detailed in previously published work⁶⁰⁻⁶³. Solid Tree Bell samples were pre-cleaned through a weak acid leach
379 and dried prior to dissolution in 7 N HNO₃. The chemical preparation consisted of a U and Th purification using
380 UTEVA (HD) or AG1-X8 (Mainz) resin through manual chemistry^{60,63}. U-series isotope measurements were
381 conducted with a semi-static multi-cup setting according to Arps⁶⁴ (HD) or Obert et al⁶¹ (Mainz). Ages were
382 calculated using the half-lives of Cheng et al⁶⁵. All ²³⁰Th/U-ages are reported relative to the year 1950 (BP).
383 Uncertainties are reported at the 2σ-level, and do not include half-life errors.

384 Major and trace element analysis

385 About 3 mg of each powdered carbonate were digested in 2 mL of 10% HNO₃ for major and trace element analyses.
386 Subsequently, concentrations of Ca, Mg, Sr, Ba, S, Fe and Mn of diluted aliquots were determined by ICP-OES at
387 Heidelberg University. Quality control of the measurement was performed using reference materials SPS-SW1 and
388 SPS-SW2 with recovery rates of ~100% for the analyzed elements. Quality control of the digestion of the carbonate
389 material was performed with analyses of parallel aliquots of the limestone reference material ECRM 752-1. The
390 recovery rate of the certified values was ~100% for the elements Ca, Mg, Sr, Fe and Mn, while a yield of ~90%
391 was achieved for the element Ba and ~80% for the element Fe. The resulting element to Ca ratios are presented
392 as molar ratios.

393 Stable carbon and oxygen isotope measurements

394 For stable carbon and oxygen isotope analyses of carbonates, approximately 50–90 µg of powdered speleothem
395 subsamples were analyzed using a ThermoFinnigan MAT253Plus gas source mass spectrometer equipped with a
396 Thermo Fisher Scientific Kiel IV carbonate device at Heidelberg University (Institute of Earth Sciences). The δ¹³C
397 and δ¹⁸O values are reported relative to VPDB through the analysis of an in-house standard (Solnhofen limestone,
398 δ¹³C_{VPDB} = +1.38 ± 0.03‰ and δ¹⁸O_{VPDB} = -4.59 ± 0.06‰) calibrated to the reference material IAEA-603 (calcite;
399 δ¹³C_{VPDB} = +2.46 ± 0.01‰ and δ¹⁸O_{VPDB} = -2.37 ± 0.04‰). External precisions (repeatable measurements of in-
400 house standard) for δ¹³C and δ¹⁸O values were better than 0.03 and 0.06‰ (at 1σ level, n >12), respectively.

401

402 **Data availability**

403 The raw data of the figures and tables presented in this paper are found in the Supplement.

404

405 **Author contributions**

406 NF, SR, WS, and NS conceptualized this study. NS conducted all analysis of carbonate and water samples and
407 performed the data quality control. SR, NS, and CS performed geochemical analysis of water samples and
408 contributed to the discussion of the geochemical data in relation to Hells Bells growth. NF, SW, DS, MW and NS
409 participated in the ²³⁰Th/U dating and quality control of U-series data and interpretation. WS and JOA provided the
410 samples and information on the Hells Bells environment. FK contributed stable carbon and oxygen isotope
411 analyses. NS and SR collected the data and NF, CS, FK validated it. All authors participated in the writing of the
412 manuscript.

413

414 **Competing interests**

415 The authors declare that they have no conflict of interest.

416

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