

Interactive comment on “A 4000-year long Late Holocene climate record from Hermes Cave (Peloponnese, Greece)” by Tobias Kluge et al.

Anonymous Referee #1

Received and published: 13 July 2020

Reviewer comment for A 4000-year long Late Holocene climate record from Hermes Cave (Peloponnese, Greece), from Tobias Kluge et al, submitted to Climate of The Past The ms from Kluge et al presents a multiproxy record (stable isotope, clumped isotopes, trace element composition) from a speleothem from Hermes cave, in the NE Peloponnese (Greece). The speleothem growth interval spans from ca. 4.5 ka to the present (though the top age is affected by large uncertainty) and thus covers a period of particular archaeological interest for the region (i.e. the late Bronze Age-Iron Age). Due to large uncertainty in the calibration, clumped isotope results are mostly used to infer equilibrium deposition. The $\delta^{18}\text{O}$ is interpreted in terms of hydrological changes (i.e. amount effect), according to previous works from the region, whereas others proxies are tentatively addressed as related to changes in hydrology, infiltra-

C1

tion and soil conditions. From the multiproxy record, authors identify a long-term trend of drying from ca. 2 to 2 ka and two events of drier conditions around 4.2 and 3.2 ka. Through comparison with others archives from the region, the authors placed the observed variability in the broader palaeoclimatic framework available for the Eastern Mediterranean. The paper is properly written and structured, and the analytical methods appear robust. However, I found the proxy interpretation very forced in some points, and not fully supported by the data. This often led to an over-interpretation of the record and to a rather speculative discussion. Also, though I appreciated the effort in trying to quantify the observed variations, I found the attempt over-simplistic, because a proper monitoring is lacking and the analyses of present-day conditions is not robust enough. Overall, in its present form the paper cannot be accepted- It should be potentially published in Climate of the Past, but only after major revision and consistent rethinking and rewriting. Please find specific comments below. Major points: Petrography: Petrographical information are totally lacking. In my opinion, they are mandatory for any speleothem research (they are also very cheap and easy to achieve!). The occurrence of specific calcite fabric (columnar) is considered the best way to assess deposition close to isotopic equilibrium (see e.g. Frisia et al., 2000; Frisia and Borsato, 2010; Frisia, 2015; Faichild and Baker, 2012. . .), whereas other fabrics were demonstrated to be affected by large kinetic effects. I strongly suggest to prepare at least one thin section (as the fabric seems quite constant) and to report proper information about it. Age modelling I do not agree with the choice of the age model: looking at Fig. S5 I found the stal-age model more convincing, whereas the bacon one shift both the lower and the upper part of the record to unrealistic older ages. I agree that it doesn't affect too much the age of the interval discussed in details, but I think the stal age one is more correct and should be used instead Equilibrium deposition and $\delta^{18}\text{O}$ interpretation The assessment of equilibrium and the determination of dripwater $\delta^{18}\text{O}$ through clumped isotopes is an interesting approach, novel but already supported by previous studies. However, its use in this work relies on just one actual temperature measurement, which is not enough nor totally significant in my opinion for quantifica-

C2

tion purposes, especially in shallow environments like this, which are likely affected by strong seasonal differences in ventilation and temperature (i.e. only 55 m from the entrance). This makes the discussion in p. 8 lines 1-11 and 26-28 and p 9 lines 1-6 and 8-24 rather speculative. Also, though I agree that clumped isotope results suggest a low degree of kinetic fractionation and that thus the speleothem $\delta^{18}\text{O}$ can be a proxy for the $\delta^{18}\text{O}$ of the precipitation, the calculation of drip water $\delta^{18}\text{O}$ based on the modern temperature is not robust enough to be presented. I agree that rainfall amount can be the main driver of rainfall $\delta^{18}\text{O}$ (and thus of speleothem) in this setting, as already shown by a number of studies and by precipitation monitoring in the region. However, this is not the only driver: changes in the seasonality would affect the final $\delta^{18}\text{O}$ and are very difficult to quantify (as correctly stated), but also changes in the source of moisture can be important, though tricky to detect. As example, in mountain regions during summer there is usually a large proportion of moisture due to local evaporation and convective precipitation, whose isotopic composition cannot be simply related to amount effect. Also, during winter, the southern Balkans are interested by incursions of cold air from NW Asia, which correlated to increased snow cover, likely influencing the annual budget and thus the mean annual value of recharge. And there are many other variables. . . The influences of these effects are often difficult to disentangle and may be contrasting or may change during time (e.g. Dragusin et al., 2014). This means that a simple quantification of $\delta^{18}\text{O}$ in terms of changes in the amount of rainfall is not straightforward and should be avoided in absence of a proper long-term monitoring of rainfall $\delta^{18}\text{O}$ values at the specific cave locations. Please add more discussion about other potential effects and remove the quantification attempt (e.g. p4 lines 4-5, pS1 lines 23-26, p 9 lines 15-16, p. 12 lines 23-32) Interpretation of $\delta^{13}\text{C}$ I found this part rather problematic. Honestly, I'm not able to see any common trend in curves presented in Fig. 5. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are not consistently anticorrelated as the paper claims, and to me their variations are largely disconnected. Also the proposed explanation for the supposed anticorrelation is not convincing at all, as $\delta^{13}\text{C}$ values always remain in a range which is consistent with biogenic input from soil (see e.g.

C3

Tremaine et al., 2011), moreover, the few examples of anti-correlation related to short infiltration times (Bar Matthews et al., 2003 but also Regattieri et al., 2018) consist in sharp opposite peaks in specific and restricted intervals of the records, and not to a slightly contrasting pattern in some points. I think the main drivers of $\delta^{13}\text{C}$ are changes in the biogenic CO_2 input and thus can be related to vegetation and soil state. The fact that they are not consistent with $\delta^{18}\text{O}$ likely means that hydrological changes were not strong enough to deeply affect the soil state. Trace element interpretation Also this part is quite problematic. Again, I do not see any clear common trend between $\delta^{13}\text{C}$ and P/Ca or between $\delta^{18}\text{O}$ and Mg, and the interpretation of the P/Ca and Mg/Ca record is a bit odd and simplistic. P in speleothem has several potential origins, depending on individual cave settings. For example, where P-rich minerals like apatite are present, it can be sourced from the bedrock and be incorporated according to a distribution coefficient in the crystal lattice as P-rich phases (Frisia et al., 2012). However, apatite is very rare. Instead, several works from temperate ecosystems indicate that phosphorus in cave drip water derives principally from the leaching of decomposing plant residue (Borsato et al., 2007; Treble et al., 2003). Thus, P concentration is often interpreted as proxy for infiltration and/or as a surface bioproductivity marker (Fairchild and Treble, 2009), with variations related to changes in vegetation and soil conditions. The fact that here its variation are decoupled from those of the $\delta^{13}\text{C}$ likely suggest the absence of major environmental variations throughout the studied period. Also the interpretation of Mg is not convincing. Due to its high solubility, it is mostly transported as solutes (Fairchild and Treble, 2009) and not within mineral detrital particle. A certain flux as solid is possible, but in this case I would expect a stronger correlation with Al and Mn, whose variations instead are largely disconnected from that of Mg/Ca. The only thing that I see from the Mg record is that there is a slight similarity in its long term trend with that of the $\delta^{18}\text{O}$ (both increasing), which may be due to hydrological variations (increased residence time during drier condition). U isotopes Also here there are some problems in my opinion. For what I know, variations in speleothem [$^{234}\text{U}/^{238}\text{U}$] can be related to changes in the relative proportion of U deriving from the carbonate bedrock

C4

versus that originating in soil (Kaufman et al., 1998; Ayalon et al., 1999; Frumkin and Stein, 2003; Hercman et al., 2020). Water interacting with more developed soil should have a higher $^{234}\text{U}/^{238}\text{U}$ content, due to greater surface of mineral-water interaction. Thus I would expect to have higher $^{234}\text{U}/^{238}\text{U}$ when the soil is more developed, i.e. under wetter conditions. Again, to me it points to a lack of major variations in soil and vegetation status during the studied period. 4.2 event: I agree that the oxygen record shows a hydrological change at that time (though not very prominent), but to me the other proxies do not, implying a very subdued expression at the cave site and a not very strong environmental response. Comparison with other records: As correctly stated, the comparison between $\delta^{13}\text{C}$ record from the Peloponnese does not show any common trend, so in my opinion figure 8 could be avoided. I also found the correlation with other $\delta^{18}\text{O}$ speleothem records a bit forced. I acknowledge some similarity in the general trend of some of the curves in fig. 9, but it is really really weak. Authors should be more honest in recognizing that most of the variations is not totally replicated, especially at the multicentennial scale. Also, why compare with the $\delta^{18}\text{O}$ record from Sofular cave? This record mostly records changes in the proportion of moisture from the Med or the Black sea, and it is not related to variations in the amount of rainfall!! The whole discussion from p 13 line 22 to p 14 line 22 about correlations with lake records etc make no sense because it is not supported by a figure. The reader must evaluate by itself the correlation among the records. The whole paragraph is advertising, not science... Other points: p1 line 22: change elemental ratios to trace element composition of to elemental/Ca ratios p1 line 25: high degree of correlation is a bit too strong, I would say similarity p2 line 11: Add However before A paleoclimate p2 line 13: This sentence reads a bit odd, please rephrase like "Here we focus on a speleothem from Hermes Cave (NE Peloponnese, Greece) and compare our record with others climatic archivers, notably speleothems and lake sediments, from the same region" or similar p2 line 23: Add a proper ref after conditions. I would also add that temperature quantification in stalagmite is often complex p2 line 28-30 I would delete the sentence about the climate divide in the Peloponnese, as this point is not further

C5

discussed. p 3 line 13: Is the vegetation totally composed of C3 plants? p3 line 25-31 it is not clear here or in the supplementary how the sensitivity of infiltration to temperature is calculated p3 line 32: Regarding infiltration as snow, I'm not very familiar with the specific cave setting, but I guess that most of the recharge is rain and not snow and that winter snow only lasts shortly, not enough to stratify in layers equilibrated and not equilibrated with the atmosphere. p4 line 7-12: Petrographical information must be added here. Also, the soot layer is mentioned here and in the abstract, but it is not further discussed in the following sections. p 6 line 25-32 I appreciate this approach and this discussion, however there is a repetition with lines 25-31 of page 4, please collate the information here or in the methods only. p7 lines 11 and 15: add the proper \pm symbol. p7 Elemental ratios: Are they molar ratios or simply element/Ca ratio with the Ca values considered invariant? Is not clear. Please explain and be consistent (and I would prefer just the element expressed in ppm and discussed as concentration, as the ratios are mostly used for elements in solution like Mg, Sr, Ba to discuss the occurrence of PCP. It would be interesting to see the value expressed as ppm, as in my experience very often elements such as Pb and Mn are very low in concentration and their changes not very significant. p7 line 26-27: I see just a slight similarity in the Al, Mn and Fe curve, not a clear correlation. A correlation table reporting r values between each pair of elements have to be inserted, and also, it would be better to plot the ratios discussed together one close to each other (see comments on figures). p7 28-29: Given that I do not see any correlation between P, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, this information about the same number of peaks is not very useful (and also a bit misleading). p7 29-30 The correlation between elevated Ba and Sr and Pb and Mn is very hard to evaluate from Fig. 5 p7 32: Can you quantify the shift and the associated chronological mismatch between the isotope and t.e. records? p8 line 2: Add the standard deviation between samples p 11 line 4-5: if Mg variations are related to hydrological variations, it makes no sense to calculate a related temperature change. Please remove.

Figures:

C6

In general they are not of very good quality. Please enlarge the y axis and make the blue bands lighter, as they actually cover the curves and make difficult to evaluate them.

Interactive comment on Clim. Past Discuss., <https://doi.org/10.5194/cp-2020-47>, 2020.