

Reply to Anonymous Referee #1

In the following we reply to the main point of criticism. Minor aspects (e.g., related to language and grammar) will be directly considered in a revised version. Referee comments are in italic and grey, the author response in black.

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, infiltration 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 3.2ka. 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.

- We are pleased by the general positive view of our study

*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.*

- A long-term monitoring does not exist, however, basic data are available from other studies (e.g., Kusch, 2000). In September 1996, H. Kusch measured a temperature of 7.6°C in the cave interior, slightly below the values measured during our cave visit in September 2017 of 8.95 and 9.2 °C at mark 19 and the deepest cave part, respectively. A large fraction of the higher temperature in 2017 may be explained by the warming global climate in the last two decades. Only the top-most part of the cave is relatively shallow (approximately 30 m below the surface). The cave levels dip with about 28-30° downwards (Kusch, 1996) with the deepest currently reachable cave part at 72 m below the entrance. Thus, the deepest parts are about 100 m below the surface. The small cave entrance at Hermes cave of only ca. 2 x1 m only allows restricted air flow. Based on the high thermal inertia of the hostrock, the cave temperature is highly unlikely to change beyond the variability known from similar cave systems (e.g., Bunker Cave; Riechelmann et al., 2011; Katerloch; Boch et al. 2010). We'll amend the manuscript with the corresponding discussion and the extra information.

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*

leastone thin section (as the fabric seems quite constant) and to report proper information about it.

- A thin section has been prepared and investigated. The manuscript will be amended by the petrographic information.

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 stalage one is more correct and should be used instead.

- Together with additional dating attempts (anthropogenic markers at the stalagmite top, e.g., C-14 bomb peak; further U-Th data for the rest and in particular the oldest stalagmite part) we'll carefully revisit the age modelling

Equilibrium deposition and $\delta^{18}O$ interpretation: The assessment of equilibrium and the determination of dripwater $\delta^{18}O$ 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 quantification 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 make the discussion in p. 8 lines 1-11 and 26-28 and p 9 lines 1-6and 8-24 rather speculative.

- Cave temperatures were already determined in the past (e.g., by Kusch, 2000; see comment above). Thermal inertia of the host rock and monitoring results from comparable systems with a few 10 meters of overburden typically yield low temperature variability on the order of $\pm 1^\circ\text{C}$ inside the cave (Bunker Cave, Katerloch, etc.). Hermes Cave dips with about $28-30^\circ$ downwards, which suggests low ventilation during summer time and some ventilation during winter.
- We'll amend the manuscript with information on temperature and ventilation

Also, though I agree that clumped isotope results suggest a low degree of kinetic fractionation and that thus the speleothems $\delta^{18}O$ can be a proxy for the $\delta^{18}O$ of the precipitation, the calculation of drip water $\delta^{18}O$ based on the modern temperature is not robust enough to be presented. I agree that rainfall amount can be the main driver of rainfall $\delta^{18}O$ (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 $\delta^{18}O$ 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 others 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 $\delta^{18}O$ 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 $\delta^{18}O$ values at the specific cave locations. Please add more discussion about other potential effects and remove the quantification attempt (e.g. p4lines 4-5, pS1 lines 23-26, p 9 lines 15-16, p. 12 lines 23-32)

- The manuscript will be rephrased as suggested. We reduce the aspects related to the quantification and add a detailed discussion about other potential effects on the oxygen isotope ratios.

- Based on IAEA isotope and rainfall data from Athens we investigated the influence of changing seasonality (Fig. S2a). We'll more prominently include this aspect in the discussion of the oxygen isotope data

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.

- Supplementary Fig. S8 shows the (anti)correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for the Hermes record as a whole. In a revised version we'll add figures focussing on specific time periods and rephrase the discussion along the lines as suggested by the reviewer

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 co-efficient 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).

- We complement the revised version with figures showing directly the relation between $\delta^{13}\text{C}$ and P/Ca as well as $\delta^{18}\text{O}$ and Mg/Ca and amend the discussion of the elemental ratios in a more comprehensive way
- We rephrase the discussion of the Mg/Ca ratios and focus on the long-term trends in consideration of potential hydrological variations

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 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}U content, due to greater surface of mineral-water interaction. Thus, would aspect 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.

- In the $^{234}\text{U}/^{238}\text{U}$ discussion we include the mineral-water interaction of the soil and the bedrock and add related references. More developed soil under wetter conditions and higher $^{234}\text{U}/^{238}\text{U}$ are consistent with our interpretation of wet and dry period in the Hermes Cave records and the measured U isotope values.

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 shows any common trend, so in my opinion figure 8 could be avoided. I also found the correlation with others $\delta^{18}\text{O}$ 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 see, 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....

- The $\delta^{18}\text{O}$ variation at 4.2 ka is the strongest signal evolution of the whole record ($>1\text{‰}$) and occurs within a relatively short time period of ca. 100-150 years. The $\delta^{13}\text{C}$ variations are linked to it and support a significant climatic effect, although it seems to have had limited influence on the elemental ratios.
- $\delta^{18}\text{O}$ variations within the Holocene and in particular during the last 6 ka are generally small in speleothems and on the order of 1-2 ‰ (e.g., Bar-Matthews et al., 2003; Zanchetta et al., 2007; Fohlmeister et al., 2012; Demeny et al., 2019). Also stalagmite records from the Mediterranean region and the Middle East reveal rather limited variations in this time period (e.g., Cheng et al., 2019). In the context of these terrestrial records a variation of more than 1‰ appears comparatively strong
- The comparison of $\delta^{13}\text{C}$ of the selected speleothems will be reconsidered and potentially shifted to the supplementary
- We'll change the presentation of the records in Fig.9 and provide a direct overlay of the Hermes Cave records with the other records. The Sofular record is in particular interesting as it shows changes in the proportion of moisture from the Mediterranean or the Black Sea and can therefore give hints on the influence of air flow from NW Asia, constraining the interpretation of the $\delta^{18}\text{O}$ signal in Hermes Cave. We'll amend the manuscript by a corresponding paragraph
- Instead of current figure 8 we'll add a figure on the comparison with the discussed lake and terrestrial records

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 discussed.

- we'll rephrase the manuscript as suggested

p 3 line 13: Is the vegetation totally composed of C3 plants?

- We didn't perform a detailed botanical survey, but due to the high mountainous location C3 plants are likely dominating.

p3 line 25-31 it is not clear here or in the supplementary how the sensitivity of infiltration to temperature is calculated

- The temperature effect on the infiltration was estimated with a first-order approach regarding the evaporation. We used the simplified connection between mean monthly temperature (T_m) and evaporation (E): $E=2*T$ (E in mm). We'll add the corresponding information to the main manuscript and the supplementary and provide an assessment of the uncertainty with respect to more sophisticated approaches

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.

- We are not aware of a detailed long-term record on snow amount and duration of snow cover, however, the existence of a skiing center close to the cave site suggests sufficient precipitation as snow during winter time

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.

- A thin section has been prepared and petrographically assessed. Related information will be added together with details on the soot layer.

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.

- We'll remove the repetition

p7 lines 11 and 15: add the proper \pm symbol.

- will be changed as suggested

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.

- We assumed that the Ca concentration is constant and assigned measured changes to analytical aspects. The elemental ratios are given in ppm/ppm. We'll add information on the concentration of each discussed element and how the measured values relate to the limit of detection.

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).

- We'll add a correlation table

p7 line 28-29: Given that I do not see any correlation between $P, \delta^{13}C$ and $\delta^{18}O$, this information about the same number of peaks is not very useful (and also a bit misleading).

- Will be reconsidered

p7 29-30 The correlation between elevated Ba and Sr and Pb and Mn is very hard to evaluate from Fig. 5

- The correlation between Ba/Ca and Sr/Ca is given in Supplementary Fig. S6. We'll add there also the relationship with Pb and Mn.

p7 32: Can you quantify the shift and the associated chronological mismatch between the isotope and the records?

- There is no chronological mismatch between the different proxies as we correlated the proxy data following the growth layer. We amend Fig. 4 with the different analyses tracks (see Fig. R1)

p8 line 2: Add the standard deviation between samples

- the standard deviation of a single analysis was 0.017 ‰ for Δ_{47} based on the replication of reference material

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. 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.

- We'll update the figures and remove the temperature calculation in relation to the Mg/Ca ratios.

Additional references:

Boch, R., Spötl, C., Frisia, S., 2010. Origin and palaeoenvironmental significance of lamination in stalagmites from Katerloch Cave, Austria. *Sedimentology*, doi: 10.1111/j.1365-3091.2010.01173.x

Riechelmann D. F. C., Schröder-Ritzrau A., Scholz D., Fohlmeister J., Spötl C., Richter D. K. and Mangini A. (2011) Monitoring Bunker Cave (NW Germany): a prerequisite to interpret geochemical proxy data of speleothems from this site. *J. Hydrol.* 409, 682–695.

Kusch, H., 2000. Die "Hermes-Höhle" auf dem Ziria-Massiv, ein korinthisch-hellenistischer Kultplatz (Peloponnes, Griechenland). *Die Höhle*, 2, 52-63.

Additional Figure

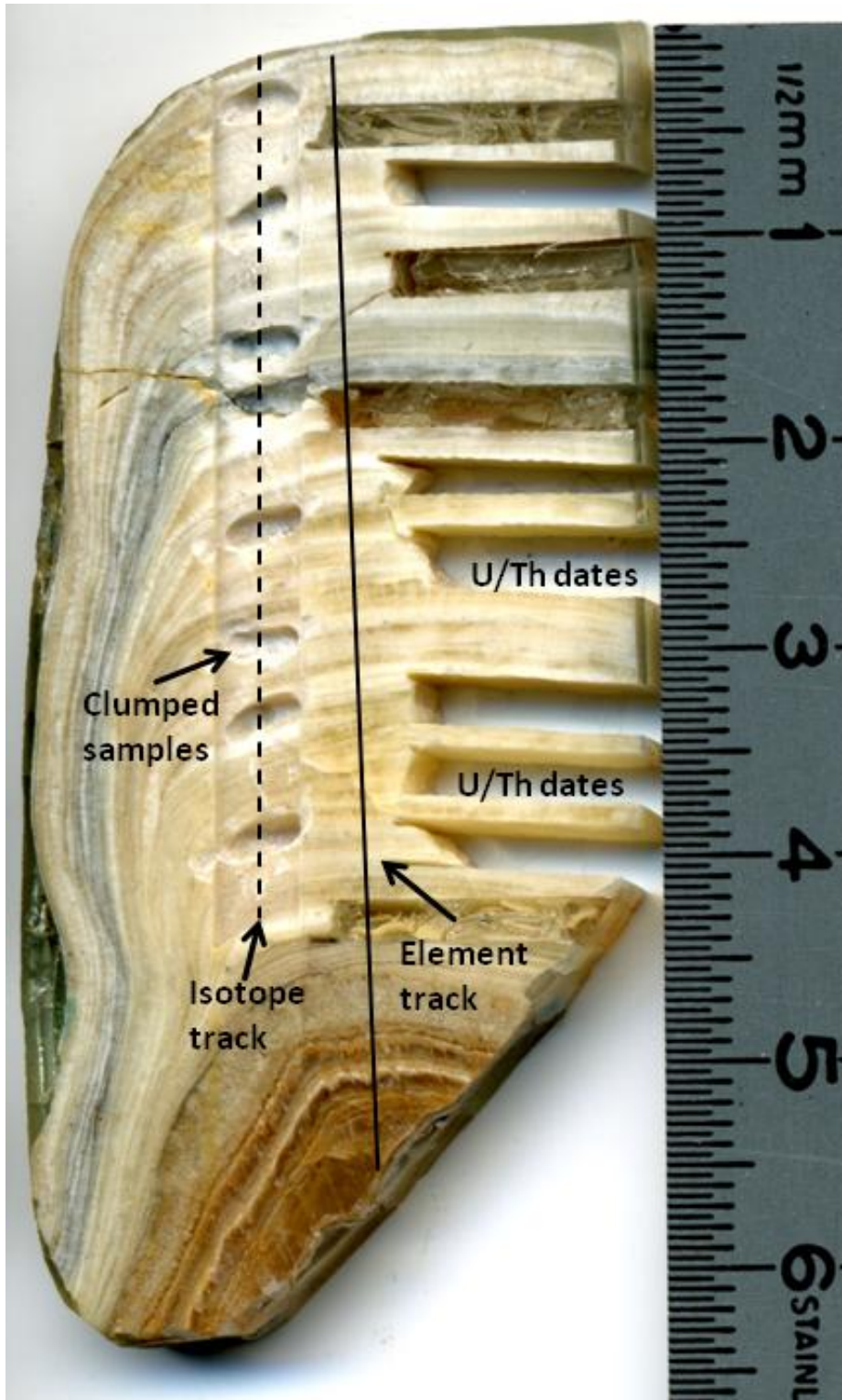


Figure R1: Spatial relation of various proxy analyses. The clumped isotope samples (deeper pits) were directly taken on the stable isotope ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) sample track that followed the visible stalagmite layering. The elemental ratios were analysed parallel to the isotope track. Samples for U/Th analyses were taken as thin blocks at the right part of the stalagmite slab. All proxies were correlated to the depth axis using the stalagmite layers as orientation.