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Interactive comment on "Aptian-Albian clumped isotopes from northwest China: Cool temperatures, variable atmospheric $p\mathrm{CO_2}$ and regional shifts in hydrologic cycle" *by* Dustin T. Harper et al.

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General Response to Reviewer Commentary

First, the authors of the manuscript entitled "Aptian-Albian clumped isotopes from northwest China: Cool temperatures, variable atmospheric pCO2 and regional shifts in hydrologic cycle" would like to thank the three reviewers for providing focused critical evaluations of our work. Below, we directly address the reviewer's comments and include the original reviewer commentary. Original reviewer comments are labeled

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Discussion paper

"RC1," "RC2," and "RC3" below. We intend on largely following the advice and comments of reviewers. In our responses, we layout specific planned revisions for the next draft submission. We are confident that we can address the reviewer's concerns with only these few, minor revisions to the manuscript. We look forward to hearing the editor's decision for the next stage of the manuscript.

Response to Review 2 (Anonymous) RC2: Harper et al. use pedogenic carbonates and paleosol elemental geochemistry to de- velop new temperature, precipitation, and pCO2 estimates of "mid" Cretaceous pale- oclimate in northwest China. They use these records to confirm previous reconstruc- tions, and to suggest that these conditions may represent examples of thresholds in shifting Hadley circulation at this time. Overall this work contributes useful new data for the region and time period, but could benefit from a refocus of the work within geographic context and with additional discussion of regional climate and potential uncertainties. Below are some comments on particular aspects of the work that could be improved or reevaluated before publication. Comments and revisions: 1) Improve editing of the manuscript throughout (incorrect agreement, missing words, etc.).

Author Response: Thank you for pointing this out. We plan to address this in the next draft submission.

RC2: 2) Is the -8.23 per mil correction for δ13Ca reasonable for this period, given the ex- istence of glendonites and the low temperatures and low pCO2? Cooler, low-pCO2 periods during the Cenozoic have substantially higher δ13Ca values (-5.5 to -6.5 per mil; Tipple et al., 2010), which may change your eventual pCO2 estimates (make them slightly higher?).

Author Response: For our study, a -8.23 ‰ correction yields δ13Ca values which range from -5.38 ‰ to -4.18 ‰ (Table 4). These values are indeed higher than those the reviewer lists from Tipple et al., 2010). Perhaps the reviewer was thinking that -8.23 ‰ was the applied δ13Ca value for all sample calculations? We can assure you this is not the case. We will more clearly lay out the applied offset and resulting δ13Ca values in the next draft submission.

If the reviewer was intending on recommending using lower values in the range of the cool Cenozoic values established by Tipple et al. (2010) (i.e., −6.5‰ to −5.5 ‰, we argue that given the relative differences in climate between the cool intervals of the Cenozoic and the cool intervals of the Cretaceous (i.e., the cool Cretaceous was likely warmer than cool Cenozoic; Hay et al. 2017; Bice et al., 2006; Westerhold et al., 2020), our slightly higher (+1.0‰ δ13Ca values are appropriate. If, however, lower values (−6.0 ‰ were applied, the reviewer is correct in stating that pCO2 estimates would tend to increase marginally.

As an example, if the δ13Ca value for sample 4-038 was adjusted to −6.0 ‰ (mid-point in the range suggested by the reviewer), the reconstructed atmospheric pCO2 value would shift from 682 to 712 ppmv.

RC2: 3) CALMAG is an elemental ratio, and should not be reported in

Author Response: Thank you for pointing this out. We plan to address this in the next draft submission.

RC2: 4) These cathodoluminescence images are concerning. High luminescence indicates substantial Mn, Fe, etc. which is usually indicative of diagenesis (e.g., Driese Mora, 1993; Budd et al., 2002), which appears to be what you sampled. Also, the final image (Figure 3, sample 6-042) is incorrectly illuminated and the bright region is just showing an incident beam from the CL (which is not calibrated across the surface). You may want to reevaluate your data to distinguish between samples selected from different regions of the carbonate nodules, and confirm that the presented data are from primary materials.

Author Response: As the third reviewer suggests, these CL images were taken with conditions for high luminescence sensitivity (e.g., He chamber). Pedogenic carbonate

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Discussion paper

nodules form during post-deposition recrystallization and hence will have features associated with this degree of alteration. High luminescence does not always indicate degree of diagenesis evidenced by the low-luminescence fracture-filled spar. This spar tended to have an isotopic diagenetic signature (lower δ18O and δ13C values) when compared to homogenous isotope values of the highly-luminescent nodule carbonate (Figure 4). In addition, the luminescence may actually be expected in these soils if they were seasonally saturated rather than a specific indication of degree of diagenesis. The Budd et al. (2002) reference that Reviewer 2 recommends describes variable luminescence in addition to discernible disequilibrium between δ13Ccarb and δ13Corg as evidence for diagenetic alteration from environmental values. Our data is rather homogenous in its luminescence and only one sample appears to have carbon isotope values suggestive of disequilibrium. This particular sample was removed from use for calculation of pCO2. However, we are comfortable including the clumped isotope temperature value because clumped isotope derived temperatures are independent of stable isotope values, so even if there was some amount of early diagenesis, it likely still represents near surface temperatures (i.e., pre-burial) as pedogenic carbonates tend to form over thousands of years (Giles et al., 1966).

We acknowledge that sample 6-042 is poorly illuminated and shows the incident beam. To address the sub-optimal quality of CL imaging in the manuscript, we intend on including new images in the next draft submission. These new images will be captured with the aim of addressing the specific reviewer concerns discussed in cathodoluminescence comments of Reviewers 2 and 3.

We do indeed evaluate our data by distinguishing δ13C and δ18O from different regions of the nodules (luminescent nodule vs. spar) in Figure 4 as the reviewer suggests. Generally, apparent secondary calcite phases (e.g., spar) are offset from the ranges in multi-spot stable isotope values of micritic, likely primary, phases of calcite (Figure 4).

RC2: 5) Why do you need Figure 6 showing different paleogeographies? Unless you add in simulations of MAT and δ18Omw as an overlay (e.g., Zhou et al., 2008;

Hasagawa et al., 2012), this doesn't really contribute to the paper. Instead just rely on Figure 7 to show what you're arguing with respect to paleogeography, and perhaps expand the discussion of this point to match.

Author Response: We argue this is an important figure for the manuscript and intend to keep it in the next draft submission for 2 reasons: 1) Allows readers to place the study location within a greater tectonic framework of the time. Including the paleogeography of the study can help readers more clearly understand paleoenvironmental setting and potential complication with regards to our interpretation of paleoenvironment 2) This figure provides a visual aid of ranges of paleolatitude for key sites in Asia for the Aptian-Albian which has not been previously done. Much of the literature which describes Aptian-Albian climate in Asia relies on these reconstructions. These studies may tend to exaggerate cool or warm conditions for a region accordingly if they do not consider all possible reconstructions.

RC2: 6) CALMAG values reported are different in the Results vs. the Discussion- does the version in the Discussion and in Figure 5 include non-B horizons? Check this and revise (or specify) as needed. The CALMAG-derived MAP fit in Figure 5 is also overly smoothed- there are not enough data points for the level of smoothing (moving average I assume?), which results in data artefacts like the curve at âĹij40m.

Author Response: In the results and Supplemental Table S4 we describe and list CALMAG values for all available samples. In Table 3 and Figure 5 (as well as in the discussion), we only include paleosol B-horizon samples which are within the range appropriate to apply MAP-calibration following recommendations by Nordt and Driess (2010). Please see section 3.3 in Results for details on how the data is presented and interpreted in the manuscript.

We agree that connecting a smooth line through the sometimes-sparse data can create artefacts, but still do argue for an increase in MAP near the end of the C10 interval as the data here are robust. For the next draft submission, we will remove the smooth fit

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Discussion paper

line for intervals of sparse data (i.e., 20-50 m and 80-100 m composite depths).

RC2: 7) You are reporting false precision in δ18Omw and temperature (and raw data tables too)- edit this to reflect precision within reported uncertainties.

Author Response: We report 1sd derived from ranges in sample measurements for our isotope values. As is, it is difficult to make the suggested edits without specific recommendations from the reviewer such as those included in the additional error propagation critiques below. Because the reviewer suggests using 2sd (2σ) for temperature uncertainty below (comment 11), we will now report temperature uncertainty in terms of 2se and 2σ in data tables and figures in the next draft submission. Reported precision in δ18Omw will be computed using 2σ temperature uncertainty. Additionally, we plan to include all of our clumped isotope output data for equilibrated gases, heated gases, standards and samples as a supplemental file in the next draft submission.

RC2: 8) Your highest pCO2 values come from samples outside the "accepted" Δ13C range for this proxy (e.g., Cotton and Sheldon, 2012). As a result, perhaps all of your es- timated values suggest low pCO2 for this period (<500ppm)? If so, does this mean C10 is non-unique, and that there is no reason to expect a shift in Hadley circulation during the mid-K? Also, why are you reporting partial uncertainties for pCO2 estimates instead of using error propagation for each component measurement (e.g., Retallack, 2009)?

Author Response: Not all of our highest pCO2 values come from samples outside "acceptable" Δ13C values following Cotton and Sheldon, 2012 (e.g., sample 3-021 which suggests >500 ppmv pCO2 prior to the C1 interval). Therefore, even if these two samples in question are removed, we still clearly observe a decline in pCO2 going into the C10 interval.

We do acknowledge that any samples utilized which fall outside of the range of Δ13C should be clearly marked as such. Following this, we plan on adjusting Figure 5 pCO2 symbols to reflect which samples lie outside this cutoff.

We decided to report partial uncertainties in pCO2 to give the reader a clearer idea of possible range in pCO2 error under two different sets of assumptions. For example, many of the calibrations which are applied to our data obtain quantitative paleoclimate parameters do not include calibration uncertainty and so this uncertainty cannot be propagated (e.g., Cotton and Sheldon, 2012). We propagate sampling and analytical error in our isotopic measurements (1sd). We then include two estimates of pCO2, one using MAP-derived S(z) values, and another under a broader range of all possible S(z) values without including assumptions regarding MAP-derived S(z) values. As S(z) values can have large impacts on resulting pCO2 records, we opt to include both approaches to illustrate the impact of the S(z) estimation strategy on our pCO2 record (i.e., sensitivity test).

We recognize that our reported pCO2 uncertainties could be improved by propagating uncertainties derived from individual components in quadrature to get a combined uncertainty (i.e., compute the square root of the sum of individual uncertainties as in Retallack (2009) as the reviewer suggests). In the next draft submission, we will include this approach to estimating uncertainty in pCO2 for each of our approaches (i.e., both for MAP-derived S(z) and large S(z) range approaches outlined above).

RC2: 9) How do your reported δ18Omw values show changes in hydrologic cycling during the Aptian/Albian? The relatively limited isotopic range (+/-2 per mil) matches the range reported from modern environments in the same region (c.f., Zhangye and Lanzhou), and MAP shows no clear trends through time (as well as a limited range of 600-1000 mm/yr). I don't see strong evidence for either changing MAP or δ18Omw across this interval (or a drop in pCO2) that would suggest a shift in Hadley Cell circulation. Are there other sites in the region to which you could compare (and perhaps make a spatial argument for the existence/location of cell boundaries; e.g., Hasegawa et al., 2012)?

Author Response: The reviewer makes a good point that while climate and hydrologic cycle variations in the C10 interval are consistent with lower temperature, atmospheric

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Discussion paper

pCO2 and perhaps shifts in the hydrologic cycle, the trends in our reconstructions tend to be washed-out, though not entirely, by uncertainty. At the very least, our study broadly captures the paleoenvironmental conditions in NW China during the Aptian-Albian, providing an important observation even without considering shorter-term variations.

We argue that higher-resolution shifts in our reconstructions likely capture an average (or seasonally consistent as discussed in the manuscript) proxy value and thus shifts cannot be appropriately compared to a modern seasonal range. While the shifts are subtle compared with uncertainty, they are consistent with carbon cycle and temperature variations for the interval and worth noting. However, we acknowledge that data from one locality is insufficient for interpreting shifts in global atmospheric circulation. Following this, in the next draft submission, we plan on toning down any language which strongly promotes the hypothesis that our records indicate shifts in Hadley Cell circulation to, for example, “may suggest” or “consistent with,” etc.

Thank you for the suggestion to compare with other sites’ data to further the argument for Hadley Cell shifts. Unfortunately, higher temporal resolution terrestrial temperature and δ18Omw water like the records published here, does not exist for the region and narrow time interval reported here. These records are the first of their kind for mid-Cretaceous Asia.

RC2: 10) What does Figure 1 show? The placement of your sampling sites relative to one another is inconsequential to this work. Could this figure be used more effectively to show relationships between White Pagoda and other studied sites in the region (e.g., for comparison in an evaluation of Hadley extent, as above)?

Author Response: Thank you for pointing this out. We appreciate the suggestion to update this figure to better show White Pagoda in relation to other studies sites of the region such as those included in Zheng et al. (2021). This will help to better place the site within the regional bio- and chrono-stratigraphic framework. We plan on updating this figure accordingly prior to the next draft submission.

RC2: 11) Something to consider, though maybe impractical for this work, is that most recent clumped isotope work suggests that <5 replicates is probably insufficient for appro- priately constraining $\Delta 47$, and that 2σ are probably more realistic for compounded uncertainties in paleotemperature estimates (e.g., Fernandez et al., 2017; Bernasconi et al., 2021).

Author Response:Thank you for the considerations. At this stage it would be impractical to return to the lab to measure more clumped isotope values on sample material. We note that 4 replicates were measured on nearly all samples (3 replicates for sample 3A-097 only). We plan on including 2σ compound uncertainties in paleotemperature estimates (text, tables, and figures) in the next draft submission as the reviewer suggests here. Additionally, in our supplemental data tables we will include the following data columns for completeness: $\Delta 47$ mean, $\Delta 47$ 1σ, $\Delta 47$ SE, $\Delta 47$ 2SE, Temperature mean, Temperature 1σ, Temperature 2σ, and Temperature 2SE.

Further, we recognize the recent and upcoming work in clumped isotope temperature calibration and correction, and plan to incorporate these approaches as necessary in the next draft submission, including approaches in propagating uncertainty.

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