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Biogeosciences Discussions



# *Interactive comment on* "Comparison of the $U_{37}^{K'}$, LDI, $TEX_{86}^{H}$ and RI-OH temperature proxies in the northern shelf of the South China Sea" *by* Bingbing Wei et al.

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Dear reviewer, Thank you for your helpful comments. We have addressed your comments and make changes accordingly. Please find related contents in the document file with changes marked.

General comments: The English in this manuscript needs to be improved to increase the readability of the text. The authors are advised to carefully review the entire manuscript for grammatical and syntax errors. Some examples of language that needs improvement are:



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Response: Thanks for the comments. In the revised version, we have checked English expression both in grammatical and syntax.

Line 35: Need to change “were synthesized" to "are synthesized.”

Response: Done. Pls see line 36.

Line 241: Authors refer to sediment trap studies (plural) but only include one reference.

Response: In fact there are numerous sediment trap studies, so we change “(Rosell-Melé and Prahl, 2013)” to “(e.g., Rosell-Melé and Prahl, 2013 and references therein)”. Pls see lines 265–266.

Awkward Syntax: Line 13-15: “The applicability of these proxies has been examined in the South China Sea, but most of these studies were focused on a single proxy and hence did not allow for a direct comparison between them.”

Response: Sentence has been rephrased as “The applicability of these proxies has been examined in the South China Sea (SCS), but only one or two of them were studied in each work. Thereby, it is difficult to make a direct comparison between these proxies in this region.” Pls see lines 13–15.

Lines 49-50: “Due to the distinctive ecology of their source organisms, these temperature proxies differ in reflecting water temperatures in terms of, e.g., water depth and seasonality.”

Response: Sentence has been rephrased as “Due to the distinctive ecology of their source organisms (e.g., depth habitat and seasonal bloom), the temperature signals from these biologically derived proxies may differ substantially between each other.” Pls see lines 51–52.

Lines 321-323: “It should be noted that it remains unclear what causes the different iGDGTs distribution between those two eco-types, and the depth boundary to separate the two, likely 200–300 m, is not exactly determined (Jia et al., 2017; Kim et al., 2015, 2016).”

Response: Sentence has been rephrased as "The difference in iGDGTs distributions between those two eco-types of Thaumarchaeota is due to the use of different enzymes for iGDGTs synthesis (Kim et al., 2016; Villanueva et al., 2015).” (Pls see line 360-361) and “The occurrence of low [2]/[3] ratios and low [Cren’] fractional abundances for most of our study sites is in agreement with the shallow water depths of these sites, as the depth boundary to separate the deep and shallow Thaumarchaeota, although not exactly determined, is likely 200–300 m (Jia et al., 2017; Kim et al., 2015, 2016).” (Pls see lines 365–367).

The discussion section on the seasonal bias of U37K’ is weak. Reported measured SSTs approach the upper limits of the Conte et al. (2006) calibration so a nonlinear relationship between U37K’ and SST is likely. Linear calibrations, including the one from Conte et al. (2006) used in this study, are hindered by a tendency to underestimate SSTs in warm regions. As such, it’s possible that the apparent bias towards production of alkenones during cool-seasons inferred from U37K’-reconstructed temperatures might be an artifact of this limitation. An example of this in the SCS is illustrated in Tierney and Tingley (2018). Furthermore, support for the authors’ hypotheses on the role of nutrients in driving the ecology of alkenone-producers in the SCS is lacking. Why not use nutrient and salinity data provided by the WOA to support your hypotheses on the effect of the PRE on the study region? According to the paper from Chen et al. (2007) cited in this study, alkenone-producer populations in the SCS are more mesotrophic-to- oligotrophic and only outcompete diatoms when nitrate concentrations are relatively depleted. Chen et al. (2007) further state that haptophyte algae populations are sensitive to water column structure, a point that you don’t consider in your discussion.

Response: Thanks for the comments. (1) We have checked the difference between linear and nonlinear calibrations, especially the BAYSPLINE (Tierney and Tingley, 2018) SST estimate. Indeed, BAYSPLINE SST estimate yields slightly higher temperature values by $\sim$0.5 °C in average than the linear calibration. But this is not against our conclusion of spring bias of alkenone temperature but reinforces it. Pls see related statements in lines 218–220 and 274–277. (2) As far as we know, the ecology of alkenone-producers in the SCS shelf is largely unknown except the paper of Chen et al. (2007). Even in that paper, the focus is on the oligotrophic basin and the relatively nutrient replete shelf is only marginally investigated. Their data showed that on the SCS shelf, coccolithophores, especially the alkenone producer E. huxleyi, were lowest during winter, when nutrients are higher, but were abundant during spring, summer and autumn. Our conclusion is basically consistent with their data. (3) The use of the water column structure, nutrient and salinity data in phytoplankton ecology studies is really a common practice. However, our study sites are mostly shallow with water depths of most of them <50 m, where water stratification does not extensively occur and WOA data fail to provide high-resolution data. So we didn't rely our interpretation on those information.

The authors' discussion on iGDGTs is also an incomplete representation of current knowledge on the TEX86 proxy. First, the authors mention that the correlation between TEX86H-reconstructed SSTs and observed SSTs could be improved with a "shallow water" calibration, yet then proceed to apply the Jia et al. (2017) calibration which is exclusively based on sediments from >329 m water depth. Furthermore, the Jia et al. calibration was calculated against water column temperatures across the upper 30-125 m whereas a number of samples in this study were collected at depths <30 m. The authors should consider re-evaluating their data using BAYSPAR (Tierney and Tingley, 2015) cf. de Bar et al., 2019 (doi:10.1029/2018PA003453).

Response: (1) The "shallow-water" calibration from Jia et al. (2017) is based on the surface SPM from 5 m water depth, thereby is really a "shallow-water calibration", but not the "sediments from >329 m water depth" as you said. We thought here you are referring to the work of Jia et al. (2012), in which they pointed out that in the SCS basin sedimentary TEX86 reflects best the temperature at 30–125 water depth. We rephrase related contents in lines 398–403. (2) We re-evaluated our data using BAYSPAR according to the comment, and did not find substantial differences. Comparatively, the local "shallow-water" calibration yielded smallest temperature residuals. Pls see our discussion in lines 392–393 and 398–403.

Second, it is well known that Thaumarchaeota inhabit a range of depths in the marine water column, but most typically reside at the base of the euphotic zone. A previous study in the SCS identified the depth of maximum Thaumarchaeotal abundance ca. 50 m (Dong et al., 2019), and line 50 of this manuscript states that iGDGTs in the SCS are likely produced between 30 m-125 m. As many samples in this study lie above these depths, it would be interesting to know how iGDGT concentrations vary across the region and how accumulation rates of sedimentary iGDGTs relate to measured TEX86.

Response: The line 50 is saying about the scenario happening in the basin of the SCS, where water depth is >300 m (Jia et al., 2012) and the finding of depth of maximum Thaumarchaeotal abundance ca. 50 m is based on iGDGT concentration in seawater SPM (Dong et al., 2019). It is really interesting to know how iGDGTs, and hence Thaumarchaeotal abundance, change with depth on the shallow shelf. We think this question could be answered by means of iGDGTs measurement in particulate matter in the water; but due to that the water depths are quite shallow (mostly <50 m) and the water are well mixed in this study region, we do not expect iGDGT concentration would change substantially with depth. We also don't believe iGDGTs concentration in sediment can do such a work, because iGDGT concentration in sediment is not only determined by Thaumarchaeotal abundance, but also controlled by bulk accumulation rate that is variable among sites. The bulk accumulation rate for each site is unknown in this study, so we are unable to relate accumulation rates of sedimentary iGDGTs with measured TEX86.

The authors also reference Zhang et al. (2017), which found that iGDGT distributions in the East China Sea from locations at <70 m water depth were significantly impacted by non-temperature influences such as nutrient from upwelling, lateral transport, or resuspension of sedimentary material. These results have significant implications for the interpretation of the data presented here, yet these factors are not thoroughly acknowledged.

Response: Lateral transport and resuspension could exert some impacts on the TEX86 proxy in shallow dynamic environment. This factor may be studied through, e.g., a comprehensive comparison between SPM and sedimentary data as did by Zhang et al. (2017). In this work, only sedimentary data were available and hence lateral transport and resuspension can only tentatively acknowledged. Pls see lines 378-382

The OH-GDGT discussion is complicated by the lack of acknowledgment that the extraction technique employed in this study may have biased the results. Yang et al. (2018) demonstrated that ultrasonic extraction of GDGTs from South China Sediments resulted in significantly lower apparent concentrations of OH-GDGTs relative to samples extracted following a Bligh-Dyer method. In Yang et al., decreased extraction efficiency of OH-GDGTs using an ultrasonic method additionally led to significant biases in SST reconstructions using the RI-OH proxy. You should acknowledge this in the manuscript in the methods or discussion sections on OH-GDGTs.

Response: In the revision we mentioned the method of Yang et al. (2018) (Lines 412–417), but we did not say more about it because it beyond this work. However, we expanded our discussion including their data and findings. Pls see related discussion in lines 418–430.

For all of the proxy data presented in this manuscript, it would be beneficial to see it placed in the context of other regional studies, similar to Figure 8. Lastly, the figures do not represent the data well and need to be updated, as do the figure captions which I also found generally uninformative. Figures 2, 3, and 4 are especially difficult to interpret.

Response: We updated figures and figure captions.

In Figure 2, the use of the same colors for both the WOA-derived SSTs and the markers related to the proxy data is confusing. This figure could be improved by splitting up the data, for example by having a 4-panel figure with 1-panel per proxy.

Response: Following your suggestions, in the revision, we made a 4-panel figure with 1-panel per proxy, and used a different color to show proxy-derived data. Pls see related changes in Fig. 2.

Figure 3 would be more useful as just a single map showing the spatial trends in the %C32 1,15 index that is referenced in Line 198 instead of plotting the fractional abundance of each of these 4 diols.

Response: We prefer to keep maps of fractional abundance of each of these 4 diols, because it is obvious to find that some C28 and C30 1,13-diols come from the discharge of the Pearl River. Together with its high positive correlation with C32 1,15-diols, these could explain the unusual low LDI values in the inshore areas. Besides, we also add a map exhibiting annual residuals in study area to better show the relation between annual residuals and fractional abundance of C28 and C30 1,13-diols and C32 1,15-diols. Pls see Fig. 4.

For Figure 4, consider averaging the fractional abundances for certain depth classes then plotting the mean for that group in a bar graph similar to your Figure 5.

Response: Thanks for comments. This is a good suggestion to make the distribution pattern of the individual iGDGTs more clear, but it may be hard to select appropriate depths. For the same goal, we split Fig. 4a into 6 panels and include data from other regional studies. Pls see related changes in Fig. 5a–5f.

Again, since both the spatial and depth patterns are important in this study, I think it would be best to plot each index in panels 4b and 4d individually as a map similar to your Figure 3.

Response: To be honest, for each index, our data only varied in a small range in the study region, with except of two samples (PRE-A8 and LD-21), which were marked in Fig. 5g–5i.

Specific comments: Line 39: Cite Kim et al. (2010) after referring to TEX86H and TEX86L.

Response: Done. Pls see line 40.

Line 40-41: Crenarchaeol has 4 cyclopentane moieties as well as the cyclohexane ring, so you should rephrase this sentence to something like "...(iGDGTs) containing 0-3 cyclopentane moieties (GDGT-0, 1, 2, 3, respectively) or 4 cyclopentane moieties with an additional cyclohexane moiety (crenarchaeol and its isomer, Cren and Cren', respectively)..."

Response: Rephrased. Pls see lines 41–42.

Line 41: Recent studies (Sinninghe Damsté et al., 2018 doi:10.1016/j.orggeochem.2018.06.005; Liu et al., 2018 doi:10.1016/j.orggeochem.2017.09.009) have determined that the crenarchaeol isomer is not actually a regio-isomer, so you should update your text by removing all instances of "regio.

Response: "regio-" was deleted in the revision.

Line 44: Though there is still a lot to learn about the biological source of LCDs, I don't agree with the statement that the source is "albeit not unambiguously identified yet" as there are several papers that have isolated LCDs in culture studies of diatoms and eustigmatophyte algae, in addition to many phylogenetic studies that link the lipids to source organisms in natural environments.

Response: We change "not unambiguously identified" to "not fully clear". Pls see line 45.

Line 45-48 Include references to Elling et al., 2014, 2015 & 2017. Nevertheless, I don't





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think you represent current knowledge on the source of OH-GDGTs fairly here. See Lipp et al., 2009; Zhu et al., 2016; Sollai et al., 2019.

Response: References were included, and we changed this sentence to "Culture studies suggest that Thaumarchaeota Group 1.1a (e.g., Nitrosopumilus maritimus) (Elling et al., 2014, 2015, 2017; Lipp and Hinrichs, 2009; Liu et al., 2012), SAGMCG-1 (e.g., Nitrosotalea devanaterra) (Elling et al., 2017), and a strain of thermophilic euryarchaeota Methanothermococcus thermolithotrophicus could synthesize OH-GDGTs (Liu et al., 2012)." Pls see our related changes in lines 47–50.

Line 167-170: As nearly half of your samples were collected in years not represented in the WOA13 V2 product, I recommend you update the manuscript with the WOA18 data that was released this summer. Furthermore, given that the studies you contrast your results to later on calculate seasonal averages from different months than those defined in the WOA product, you should use the monthly data from the WOA18 instead of the pre-defined seasonal means to strengthen the comparisons you draw in the discussion section.

Response: Thanks for comments. We updated the MS with WOA18 data. We prefer to use the pre-defined seasonal means in WOA product, because after comparing monthly mean SST in studied sites, we find that three coldest months are from Jan to Mar and warmest months are July, August and September. The definition method of 4 seasons by WOA18 already better reflect the seasonal variance of SST in this study area.

Line 177: You use the acronym “WD" yet this acronym was never defined previously in the text.

Response: Defined. Pls see line 93.

Line 205/Section 3.4: You should separate the results related to iGDGTs and those related to OH-GDGTs.

Response: Separated. Pls see.

Line 223-224: Are these relationships significant?

Response: p value was added. These relationships are very significant. Pls see related statements in lines 414–415.

Line 233-234: Why do you refer to the Chinese Marginal Sea here instead of the South China Sea?

Response: There is no local RI-OH-SST calibration for the SCS. However, the calibration proposed by Lü et al. (2015) is based on data from both East China Sea and South China Sea, which together is called the Chinese Marginal Sea.

Line 235-236: It is confusing that you refer to residuals here when the figure you reference (Fig 2) does not show the Proxy-Obs. SST residuals.

Response: In the Fig. 2, we only can see the difference between proxy-derived and observed SST. So we changed "Fig. 2 and Suppl. Table 5" to "Suppl. Table 5".

Line 239: Include references to culture studies that support this statement.

Response: We added references "(Conte et al., 1998; Prahl and Wakeham, 1987; Prahl et al., 1988; Sawada et al., 1996; Volkman et al., 1995)". Pls see lines 266–267.

Line 244-245: You really should discuss why you think your results indicate that U37K'-SST are biased towards spring temperatures as there is nothing in Figure 2 that demonstrates this. You could do a simple linear regression between U37K'-derived temperatures and seasonal SSTs and if there is a significant relationship with observation spring SSTs, then your claims are valid.

Response: Thanks for the comments. We thought that here you want to say "do a simple linear regression between U37K' index and seasonal SSTs". This method is really a common practice, but in our study region, spatial SSTs in each season varied in a very small range, with the largest in winter but still <6 °C. Together with influences of factors other than SST on proxies, this usually leads to poor SST-proxy correlations for all seasons, albeit slightly better for winter data. So we did not use correlation as a criterion to decide seasonality. Instead, we used another common criterion, i.e., temperature residuals between calculated temperatures from established calibrations and measured seasonal SS. We used this method for consistency in the whole paper. Pls see related statements in lines 195–199.

Line 270: Either here or in the methods section you should provide more details on how you conducted this statistical analyses.

Response: We added details in method section. Pls see our related statements in lines 138–141.

Line 279: Based on your above discussion on the different sources of these three lipids and the results of the previous studies on LCD distributions in coastal environments that you cite, this supposition about an opposite relationship between C28 1,13, C30 1,13, and C32 1,15 diols and temperature is unlikely and seems unnecessary to include.

Response: This sentence was deleted.

Line 285 - 287: The statement explaining why a threshold of %C32 1,15 <20% was used from Lines 288-290 should be moved here.

Response: Sentences have been rearranged. Pls see lines 313–315 and 317–320.

Line 305: Replace "methane-related" with something more accurate such as "...iGDGTs from archaea involved in methane cycling..."

Response: Replaced. Pls see lines 341–342.

Line 306: Please indicate what "substantially elevated" values for the [2]/[Cren] and [0]/Cren indices are as you do for the MI.

Response: "substantially elevated" values for the [2]/[Cren] is >0.2, and [0]/[Cren] indices is deleted from here. Pls see line 340.

Lines 309-312: Another paper you cite elsewhere in the text, Zhou et al. (2014), concluded that brGDGTs in the PRE are also likely derived from in situ production in the river rather than solely originating from erosion of catchment soils.

Response: The ability of the BIT index to indicate soil input in this region has recently been discounted by finding that branched GDGTs may be aquatically in-situ produced (Zhou et al., 2014). Nevertheless, considering that the sample PRE-A8 is located at the upper river mouth, together with the highest %C32 1,15 values as discussed above, we believe iGDGTs may be impacted to some extent by terrestrial input. Pls see related statements in lines 345–3448.

Line 321-322: The difference in iGDGT distributions between 'deep' and 'shallow' Thaumarchaeota eco-types is due to the use of different enzymes for iGDGT synthesis (cf. Kim et al., 2016 doi: 10.1016/j.gca.2015.09.010; Villanueva et al., 2014 doi: 10.1111/1462-2920.12508).

Response: Changed. Pls see lines 360–361.

Line 339-343: In Kim et al.'s 2008 paper, the authors note that the difference in their TEX86 calibration for core top sediments from depths <200 m relative to the calibration for the entire data set is negligible, likely because contribution of iGDGTs from deep dwelling archaea to the sediment floor is minimal relative to the contributions from shallow-dwelling Thaumarchaeota, a point that has been highlighted in many other studies. As such, I don't believe this is the cause of the mismatch between the TEX86H-reconstructed temperatures and observations you report in your manuscript.

Response: We note that the influence of water depth on the TEX86 proxy have not reached an agreement. The contribution of iGDGTs from deep dwelling archaea to the sediment floor has been estimated to be >50% in the deep seas (e.g., Kim et al., 2016; Jia et al., 2017), although the abundance of Thaumarchaeota and GDGTs have been found maximum at the lower euphotic zone. We thought the contribution of deep dwelling archaea might be a background for sedimentary GDGTs in a specific site, where TEX86 could be mainly controlled by the variable shallow-water iGDGTs. Nevertheless, when considering spatial distributions, the contribution of the deep dwelling archaea could change some extent, which may be a cause of the significant TEX86-SST scatters. Of course, these are beyond this paper, and we did not say more about that in the paper. Kim, J.-H., L. Villanueva, C. Zell, and J. S. Sinninghe Damsté (2016), Biological source and provenance of deep-water derived isoprenoid tetraether lipids along the Portuguese continental margin, Geochim. Cosmochim. Acta, 172, 177–204. Jia, G., X. Wang, W. Guo, and L. Dong (2017), Seasonal distribution of archaeal lipids in surface water and its constraint on their sources and the TEX86 temperature proxy in sediments of the South China Sea. J. Geophys. Res. Biogeosci., 122, 592–606.

Line 390: In Line 315 you draw the opposite conclusion that your samples are not appreciably impacted by TEX86H?

Response: We suspect "TEX86H" could be "by soil input". Our opinion is that judged from the BIT value, the sample of PRE-A8 is influenced by soil input (Lines 345–347). However, [Cren'] data could also suggest the predominance of Euryarchaeota (Lines 354–357) for the sample. We think this is not controversy as the two factors may co-occur at this site.

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