

Interactive comment on “Ubiquitous production of branched glycerol dialkyl glycerol tetraethers (brGDGTs) in global marine environments: a new source indicator for brGDGTs” by Wenjie Xiao et al.

Anonymous Referee #2

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The paper by Xiao et al is a very interesting and valuable contribution to the study of the distribution and origin of branched GDGTs (brGDGT) in mesophilic marine environments and their use as climate proxies. The authors show, initially for the Bohai Sea and subsequently in an extensive data set, that the ratio of two branched GDGTs (termed IIIa/IIa) are dependent on their geographical location. So that values of the ratio in continental sites, coastal environments and marine settings span, generally (as the authors themselves state in multiple occasions), different range of values. This finding, in my opinion, should grant the paper publication in a number of (bio)geochemical journals, as the data and method seems very sound, and the sample set, together with

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the use of bibliographic data, are very comprehensive. One should congratulate the authors for such a compilation of data.

The paper is in general well written and presented although there are a number of spelling and grammatical mistakes that still need to be addressed to achieve that the language is fluent and precise.

Any of my concerns with the paper derive from the interpretations and implications that the authors derive from their observations on the distribution of the IIIa/IIa. Some of their interpretations are just hypothesis, but are treated as facts as the paper progresses so that the conclusions contain a number of statements that are not backed up by the data.

Unlike what is claimed in the paper, the authors do not provide proof that in situ production of brGDGTs is actually taking place in marine settings. This is just their hypothesis, albeit plausible, to explain the observed distribution of IIIa/IIa values in the Bohai sediments and other marine settings. Consequently, the paper should be revised to differentiate between actual findings (i.e. IIIa/IIa values), and their proposed interpretation(s) to explain the geographical distribution of the data values. Moreover, it is always useful, when interpreting data, to consider alternative interpretations, if only to discard them and test the strength of the apparently most plausible proposition. For instance, have the authors consider the role of hydrodynamically sorting in explaining IIIa/IIa values in marine settings?. Particles of different sizes may contain different compositions of lipids, and thus sediments change in composition with distance from shore in parallel with changes in particle size.

In this regard, in the title and Conclusion, the authors cannot claim that “in situ production of brGDGTs in marine environments is a ubiquitous phenomenon”, because this is an interpretation that they reach to explain why brGDGTs IIIa/IIa ratios have different values in continental, coastal and marine sediments. No other alternative explanations are explored, and no evidence is produced that actual in situ production of

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brGDGTs is occurring. At the moment it is a plausible hypothesis, but not a fact. This confusion between hypothetical interpretations and facts is particularly acute in the following statement in the conclusions: “in situ production. . . is particularly important for those marine sediments with low BIT index (<0.16) where brGDGTs are exclusively of a marine origin.” No evidence is produced to demonstrate this statement. Similarly, the authors do not prove that “the IIIa/IIa values. . . in marine sediments reflects an influence of pH rather than temperature on the biosynthesis of brGDGTs by source organisms.”. No data, including measures of pH in the samples, are made available to prove such a claim.

The authors also make extensive use of the BIT index throughout the paper. Given that such an index is used to evaluate the information and possible applications of the IIIa/IIa ratios, the authors should thoroughly discuss the pros and cons, or rather limitations of the BIT index. However, the discussion of this index fails to acknowledge, except as an afterthought in the last line of the paper (li 363), that BIT values are not just dependent on the inputs of soil brGDGTs, but also on the productivity of marine Archaea, which is linked to a large extent to marine productivity. For instance, sites with equal inputs of terrestrial brGDGTs but different local productivity would display different BIT values. In my opinion, the extensive discussion of figure 6, which leads to the generation of figure 7, is meaningless unless proper appraisal is made of what BIT values variability actually means, and proper consideration is made of how changes in productivity influence BIT. It should also be noted that iGDGTs, and chrenarchaeol, are found in soils.

Below some more detailed comments.

Lines 34 and 35: to estimate environmental variables in the past

Line 45: the attribution of the brGDGTs is still hypothetical. But in any case it is unclear why the authors claim that their preferential occurrence in soils/peats means that they are derived from bacteria

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Li 48-50: the text should be rewritten, it is unclear what the authors are trying to say

Li 58-59: the BIT index is used for what?

Li 58-60: in here the authors should also comment the often overlooked drawback of the BIT index, namely that is dependent on the input of chrenarchaeol, which is linked to marine productivity. Consequently, BIT values are not just dependent on the inputs of soil brGDGTs, but also on the productivity of marine Archaea. For instance, sites with equal inputs of terrestrial brGDGTs but different local productivity would display different BIT values. There are a number of references out there discussing this issue, for instance:

*Herfort, L., S. Schouten, J. P. Boon, M. Woltering, M. Baas, J. W. H. Weijers, and J. S. Sinninghe Damsté (2006), Characterization of transport and deposition of terrestrial organic matter in the southern North Sea using the BIT index, *Limnol. Oceanogr.*, 51, 2196–2205, doi:10.4319/lo.2006.51.5.2196.

*Fietz, S., Martínez-García, A., Huguet, C., Rueda, G., & Rosell-Melé, A. (2011). Constraints in the application of the Branched and Isoprenoid Tetraether index as a terrestrial input proxy. *Journal of Geophysical Research*, 116(C10), 1–9.

*Smith, R. W., Bianchi, T. S., & Savage, C. (2010). Comparison of lignin phenols and branched/isoprenoid tetraethers (BIT index) as indices of terrestrial organic matter in Doubtful Sound, Fiordland, New Zealand. *Organic Geochemistry*, 41(3), 281–290. <http://doi.org/10.1016/j.orggeochem.2009.10.009>

Li 76: “The premise of all brGDGT”, do you the authors mean: the underlying assumption?

Li 79: “supporting in situ production of brGDGTs”: the authors cited hypothesized the occurrence of in situ production, so their studies supported the hypothesis of the occurrence of..

Li 89: instead of “supported” use “findings were coherent with the hypothesis that

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brGDGTs are in situ produced in marine environments”.

Li 91: instead of “river” use “fluvial inputs or run off”

Li 93-94: brGDGTs have not been analyzed in that many dust samples to date, but it may be obvious to assume in the meantime that their concentration in dust will be as high, proportionally, to the contents of soil particles in dust. In this section it is relevant to cite as well the just published paper by Yamamoto et al., 2016, GCA, 191, 15 October 2016, Pages 239–254.

Li 95: “became”: why just in the past?

Li 112: mean depth

Li 115-116: One 64 cm long gravity core

Li 117: namely?

Li 121-122: I would rephrase “cores cover the sedimentation period of less than 100 years”

Li 125: samples were ground with a mortar and pestle

Li 137: Define “EtOAc”

Li 138; I would rephrase “Samples were injected...”, where?

Li 139: As this is relatively novel, I would indicate from which reference(s) the HPLC method is derived.

Li 175: “The dataset in this study are composed of GDGTs from..” absolute/relative concentrations?, fluxes?

Li 177: I would rephrase “and have water depth”

Li 197: I would rewrite “Both iGDGTs including crenarchaea and brGDGTs”. Chrenarchaea or chrenarchaeol?

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Li 206: “expectable”?

Li 207-210: iGDGTs are found in soils too.

Li 208: the statement does not make much sense as the BIT was not “designed” for this purpose as it has already been discussed

Li 212-214: I would rephrase this section “all parameters except MI can distinguish Chinese soils from Bohai Sea sediments”

Li 234-235: “enhanced IIIa/IIa values in the Bohai Sea sediments is caused by in situ production of brGDGTs.” The statement should be rephrased to differentiate between actual findings (i.e. IIIa/IIa values), and their proposed interpretation(s) (i.e. in situ production).

Li 237-239: “The site M1 is adjacent to the Yellow River mouth and receives the largest amount of terrestrial organic matter, causing lower IIIa/IIa values”. Again, the authors should rephrase the statement to indicate which is their interpretation of the IIIa/IIa values, as they do not prove what causes the lower IIIa/IIa values. The same applies to text in lines 262, 272-273, 315, 371-374.

Li 240: “comprises of the least amount of terrestrial organic matter”, please justify this statement

Li 242: “strongly”, why?, is this a subjective claim or is backed up by some stats.?

Li 246-247: The authors should indicate that they try to validate the ratio as a proxy for something, not to validate the ratio itself, or are they also trying to assess if the IIa and IIIa are ubiquitous?

Li 258: compiling or compilation?

Li 259: brGDGTs concentrations?, fluxes? Data?

Li 274-275: I would rephrase this section

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Li 275: Where is the statistical analysis?

Li 278: "unusually low" in which context are they low?

Li 279: "Bab el Mandeb" strait

Li 279: "litter" or low?

Li 280: salinity, no units?

Li 281-283: The Red Sea is an extreme environment?, the authors do not explain why the ratios from environments as different as those in Fig. 5 (e.g. Arctic, Mediterranean, Chilean margin, South China Sea, river waters and soils) fit within the scheme proposed to interpret the IIIa/IIa ratios, whereas the Red Sea does not. The interpretation proposed is not very convincing, particularly as they seem to argue through the text that the producers of brGDGTs in soils and marine settings are not the same type of organisms.

Li 284-286: level or values?

Li 290: "Why do soils have lower IIIa/IIa" and the Red Sea?

Li 302-303: Please explain further what is meant by and why is not related to the IIIa/IIa ratio: "because both soils and marine sediments are globally distributed and their temperatures (MAT vs. sea surface temperature) have no systematic difference".

Li 305: "positive correlation with soil pH ($R^2=0.43$)", really?, with such a R^2 value?

Li 305-312: I would use more caution in this section as most of the evidence used to back the authors' interpretation is hypothetical

Li 322-324: the regression in Fig. 6 is the product of wishful thinking. One can fit any curve to a group of unrelated data point and get "satisfactory" R^2 value. I think that it is evident from Figure 6 that BIT and the III/II ratios are unrelated. There are two cluster of data. Why samples with BIT values below 0.3 (which are supposed to be only typical

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of sites with low terrigenous inputs) have such an spread of III/II values?, Similarly, how come that values of III/II below 0.8, which are proposed to be only found in soils (li 285) has such an spread of BIT values from 0 to 1. It does not make sense to me if both indicators are indicators of marine vs. terrigenous organic carbon. Should not they fit into a simple straightforward linear regression if IIIa/IIa and BIT are both indexes for assessing soil organic carbon (inputs) in marine settings, as claimed by the authors? .

Li 366-368: it is not necessary to say in the conclusions section that the authors have reached some conclusions. It is redundant.

Li 369: Please define what is meant by "generally lower", as it stands it is a subjective statement which is followed by values that are purported to reflect objective thresholds (which are not in fact).

Li 369-370: The authors have not demonstrated the occurrence of terrestrial inputs in all samples studied (e.g. Fig. 6). They cannot claim that high values of III/II occur in sediments "devoid of significant terrestrial inputs". What is meant by significant anyhow?.

Fig. 1: m/z of chrenarchaeol?

Fig. 4 combines 4 graphs extracted from published papers that are unrelated to each other, and I think that they should go in different figures for coherence sake in the supplementary information section. Explain the abbreviations in the x-axis in fig. 4b in the legend.

Fig.5. The use of symbols of different size prevents the visualization of all the data in the map, as the big dots cover smaller dots, and also are easier to visualize than smaller dots, giving the impression that "there are more of them". Please use another way of visualizing all the data that provides equal weight to data with different range of values.

Table 1: where are the samples from?. Please explain further what is mean by: "Differ-

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ent letters (a, b, c, d) represent significant difference at the level of $p < 0.05$.”

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