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Biogeosciences Discussions

Interactive comment on "Reconstruction of the biogeochemistry and ecology of photoautotrophs based on the nitrogen and carbon isotopic compositions of vanadyl porphyrins from Miocene siliceous sediments" *by* Y. Kashiyama et al.

Y. Kashiyama et al.

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We acknowledge the reviewers for their thoughtful comments and suggestions. We have implemented most of their suggestions. All the technical corrections of both referees were now reflected in the revised manuscript. Below, we only respond to the general and specific comments from two referees.

1. Responses to the comments of Anonymous Referee #1:

>The authors have made similar observations and reached similar conclusions for Cretaceous OAEs. Some discussion on how their Miocene data/interpretation compares

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with those of Cretaceous OAEs, or at least some reference to it, would have been nice.

We newly mentioned to Kashiyama et al. (in press) section 4.3 and therein made a brief discussion on the common significance of diazotrophic cyanobacteria in the Onnagawa basin and Cretaceous OAEs as well as Mediterranean sapropels.

>Has there any previous study been done on hopanes in this formation? If large amounts of 2-methylhopanoids have been found than this would support the conclusions of the authors.

So far no report has been made on 2-methylhopanoids from the Onnagawa Formation. We also did not found any significant amount of 2-methylhopanoid from our samples. We think that 2-methylhopanoid-free cyanobacteria were probably responsible for the production in the Onnagawa since these compounds were not actually found in a half of cyanobacterial species.

>l. 7., p. 362: is it chlorophylls c or chlorophyll c?

It should be "chlorophylls c" since it refers to three homologous compounds: chlorophyll c1, chlorophyll c2, and chlorophyll c3. We now refer to them as "chlorophylls c1-3" on the first appearances in each section.

>l. 10, p. 364. Any reference which supports this statement?

Following the advice, we made reference to Ohkouchi et al. (2006, in press) here.

>l. 2, p. 366: ...ecology of photoautrophs in the Miocene Pacific Ocean...

The Onnagawa basin was not a part of the Pacific Ocean but a temporary-existed back-arc basin during the formation of Japanese Islands. We thus changed to be: "...ecology of photoautrophs in a marginal basin of the Miocene Pacific Ocean".

>l.21, p. 370: You combined results and discussion but in effect 3.1 is the Result section and the following paragraphs are discussion. You can divide up the paper like this.

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In the revised manuscript, we assigned the whole section 3.1 of the original manuscript to be the section "3. Result". Accordingly, we brought the original sections 3.2, 3.3... into section "4. Discussion" as sections 4.1, 4.2..., respectively.

>l. 5, p. 372: You can add a sentence ruling out isotopic fractionation due to removal of the carbon atoms. You have done this for the other isomers.

We actually did so in the original manuscript. In the first paragraph of Section 4.1.2, we noted that "... ethyl groups that are lost from the C-3, C-8, or C-17 positions (3-, 8-, and 17-nor DPEP, respectively) are equivalent ... originate in the two methylene carbons of the carboxyethyl group of Uroporphobilinogen..." Thus, the observed isotopic differences among these species of porphyrin cannot be explained by the loss of these equivalent carbon atoms.

>l. 21, p. 372: Are this values really statistically significantly different considering the analytical error of +/- 0.3 per mill? Perhaps a statistical test showing this would be nice.

We added data on statistical tests (Student's t-tests) in Supplementary Materials (Table S1 and S2), which supports our claims at a significance level of 0.05.

>l. 15, p. 377: What is the standard deviation of this 4.8 per mill average? This should be added to the uncertainty in reconstructing the original 15N.

The standard deviation of this value is already described in introduction (1.4permil; 1s, n=20). We further noted on the effect of this possible uncertainty in this paragraph as: "It should be noted that there are some uncertainty in these reconstructions due to the natural variation in d15N difference between the chlorophylls and the cell (+/-1.4permil; 1s, n=20); hence, the estimates may be somewhat wider ranges than these values."

>l. 9, p. 379: Some explanation of this procedure would be beneficial as it is not clear from Table 4 how it is calculated.

We added detailed description for estimation of ep values in the Supplementary Materials. In the footnote of revised Table 4, we omitted a phrase mentioning to paleo-

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pCO2, which was mistakenly left when the table was made by modifying a table in Kashiyama's PhD thesis but is now irrelevant to the content of the present table. Accordingly, we omitted one reference (Tajika, 1998). We also fixed minor mistakes in the Table 4 (db/c and dc/d in the footnote must be eb/c and ed/b, respectively).

>l. 11, p. 380: Pancost et al did not look at carboxylases but inferred this to explain the small ep.

We removed Pancost et al. (1997) from the citations here.

>l. 17, p. 381: Explain why 24-norcholestane suggests diatom productivity.

Here is our English problem. We tried to say that Suzuki (1993) suggested diatom production based on his finding of high abundance of 24-norcholestane, and thus it is not our original interpretation. We thus rephrased the sentence.

>l. 6, p. 382: Statistically significant?

Changed to be "...demonstrated slight but statistically significant differences."

>Table 1, footnote: What does it mean that III, IV, and V are "continuous" samples?

We meant that these samples were stratigraphically adjacent each other – single specimen (BA140a) was subdivided based on lithological changes. However, biogenic silica content reported by Tada (1991) was determined only for the whole specimen. The original footnote was intended to explain why only one value of silica content is given for these three samples. In the revised manuscript, we removed the second footnote of Table 1, because it is neither mentioned in the main text nor relevant to the discussion. Instead, we added some explanations to the first footnote on the biogenic silica content of BA140a.

>Fig 4a. Why were the values not plotted relative to DPEP like in fig 4b?

These plots illustrate only isotopic relationships that are discussed in the text. We avoided plotting all the relationships in these figures so as to keep the figures easy to

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see. Instead, all these isotopic relationships are shown in Figs. S1 and S2 in Supplementary Materials. Therefore, we made only minor changes in Figs. 4a and 4b following the Referee #2's comment discussed below.

1. p. 363, lines 19-20 "...thereby exclusively recording the signal from the marine environment." It would probably be more correct to replace "marine environment" with "euphotic zone" as there could be deep water processes that are not recorded in the pigments, particularly in a stratified basin where there is little exchange between layers. It is possible to record deep water processes in the chloropigments, but only when the isotopic signals of these processes reach the surface waters.

Here, we meant "marine environment" as opposed to "terrestrial environment". In this paragraph, we claimed that the porphyrins preserved in marine sediments were not derived from land plants, hence not recording terrestrial processes. Therefore, we instead rephrased it as "...thereby exclusively recording the signal from the marine primary production."

2. p. 363, line 28-p.364, line 2 While I understand why the Chikaraishi et al., 2005b paper is cited, I am not sure your sentence accurately conveys your point that terrestrial input was minor. It might be better to indicate whether the small amount of chlorophyll/chlorophyll products present was proportional to the primary productivity in the lake.

We missed an important word here, which apparently caused the referee's confusion. We meant "...Chikaraishi et al. (2005b) reported that chlorophylls and their degradation products originating from terrestrial plants were present in only minor amounts in a small lake with a high flux of organic matter from the surrounding forest." Chikaraishi et al. (2005) concluded that chlorophyll and chlorophyll products in the lake was mostly from aquatic phototrophs.

3. P. 364, line 10-18 While the N isotopes may not change, there is a possibility for the C isotopes to alter in degradation. You might also consider stating Sachs' d13C and

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d15N values for chlorophyll as well to show that the N signature does not significantly change during degradation.

As the referee pointed out, Ohkouchi et al. (2008, in press) noted that d13C of DPEP and more dealkylated sedimentary porphyrins may slightly altered from that of precursory chlorophyllide after removal of a few carbon atoms (e.g., C-133 and C-173 positions) because of intermolecular isotopic heterogeneity. However, considering relatively a large number of carbon atom of the porphyrin (32 for DPEP), such an effect should be considerably small so that we think it does not significantly affect our interpretation. In the revised manuscript, we also cited Sachs et al. (1999) here.

4. P. 364, line 26 Do you mean "depleted" in an isotopic or a concentration sense? I suggest replacing the word "accessed" with "made biologically available".

We mean depleted in a concentration sense, so we made a change as advised.

5. P. 366, line 1-2 "...biogeochemistry and ecology of photoautotrophs." Please qualify that your conclusions are for this site and Miocene time frame only.

We rephrased as "...biogeochemistry and ecology of photoautotrophs in a marginal basin of the Miocene Pacific Ocean."

6. P.367, line 16-p. 368, line 2 I assume this paragraph summarizes the method as explained in Kashiyama et al., 2007a. If so, I don't think this paragraph is necessary. I suggest citing the paper, then describe the update to the method. Also, what was the mass of sediment used for each sample?

We rephrased the entire paragraph following the advice of the referee. We also described the mass of sediment used (˜0.5 kg for each sample).

7. What was the percent as porphyrins of the total nitrogen and carbon in the sample? This might be useful to report for comparison to other studies.

Each sample contains approximately 40 nmol of vanadyl porphyrin (VOP) per 1 g of

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sediment. Therefore, VOP-nitrogen per TON and VOP-carbon per TOC ranges roughly 0.15-0.55% and 0.05-0.15%, respectively. In the revised manuscript, we noted concentration of VOP.

8. P.371, lines 11-13 I'm not sure the data support the idea of "regular isotopic relationships", as the d13C and d15N numbers are rather large for some of the porphyrins, particularly 8-nor-DPEP when compared with 17-nor-DPEP. The d15N for that relationship has a range of ˜6 per mil, which (if seen in a bulk sediment d15N profile) could indicate a very large environmental change. The relative relationships between porphyrins in the same sediment layers (BA vs. GJ) seems more consistent, so maybe it would be better to compare porphyrins only within the same layer?

Here, we intended to suggest that the distribution patterns of isotopic difference are different for different species of porphyrins. As noted by the referee, however, "regular relationships" may be not the best wording here, particularly because of relatively large variation of 8-nor-DPEP. Therefore, we rephrased as "Certain isotopic trends were observed..." The large d15N variation of 8-nor-DPEP may be due to environmental instability for the habitat of the source organism, possibly Prochlorococcus (see our reply to the comment 14.). In the future study, we would like to elucidate what the isotopic signature of 8-nor-DPEP represents through, for example, taxon-specific (e.g., Prochlorococcus) isotopic studies for the modern photoautotrophs as well as investigation of its stratigraphic variation (see our reply to the comment 14.). In Fig. 4 of the revised manuscript, we plotted with different symbols for the data from each sediment layer (BA vs. GJ). In fact, the isotopic relationship for cycloheptanoDPEP is somewhat more consistent within the same layers. However, the overall trends are very similar, so it does not significantly influence to the discussion here.

9. P. 372, line 4 "...significant enrichment of 13C..." I assume you mean "mathematically significant" rather than significant in magnitude, since the difference in d13C between the average 17-nor-DPEP and DPEP is less than 1 per mil. Reporting the numerical values for d13C and d15N also might be useful here.

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Yes, we meant "mathematically (statistically) significant". We change the word in the text and cited the statistical test in Supplementary Materials. We also reported the numerical values for d13C and d15N in Supplementary Materials (Table S1).

10. P. 372, lines 3-5 Is there a possibility that the isotopic signal or 17-nor-DPEP reflects a mixture of origins (i.e. both from chl c and from other non-specific means)? The 17-nor-DPEP and DPEP d13C values are very similar (especially considering the DPEP sources are non-specific), and there is no other information given that would eliminate the non-specific degradation pathway from contributing to the 17-nor-DPEP pool. You may be able to support your conclusion better with a quick mass balance.

As discussed in the later part of the manuscript, we think the majority of DPEP as well as 17-nor-DPEP were derived from diatoms (suggested by other geological data); namely, the former was derived from Chls a and c, and the latter was derived from Chls c only. There was thus only minor contribution of other source to DPEP, which resulted in slight isotopic differences between these. Considering its structure, non-specific degradation cannot be a major process pathway for the 17-nor-DPEP, if any, particularly when there was such massive production of Chls c by diatoms. Because can neither constrain the difference in preservation potentials among these pigments nor estimate isotopic value of unknown "other sources" than diatoms, it is not possible to make a meaningful mass balance calculation.

11. P. 373, lines 20-22 Would the rarer pigments also explain the wide range in isotopic values? If the pigment incorporates nitrogen in the same manner, why is there such a large range?

We speculate that the wider range in isotopic value may reflect wider habitat of Prochlorococcus. Because Prochlorococcus is adapted to relatively deeper water enriched with blue light (400-500 nm), their isotopic signature should reflect those of nitrate/ammonium in deep water, which could be widely variable under the influence of variable extent of denitrification in such an anoxic basin as the Onnagawa. Thus, it

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could be differentiated from the majority of photoautotrophs dwelling in the shallower environment with supply of nitrogen from N-fixation. In the revised manuscript, therefore, we added a sentence suggesting a possible cause of the isotopic variation.

12. p. 376, lines 19-25 You might want to emphasize that the spatial variation in grazing you are referring to is with regards to depth (z direction), not latitude/longitude (x/y directions).

Following the advice, we revised as: "...photoautotrophic populations would have varied spatially (i.e., variation along depth) and...".

13. Are there any other biogeochemical marker studies to support your conclusions of a highly stratified water column with anaerobic bottom water conditions?

We think that this is the first strong evidence for highly stratified water column for the Onnagawa basin, although many works has suggested presence of anoxic bottom water.

14. I would have liked some additional explanation of the variations in isotopic values for porphyrins with depth and between the Horizons. Many of the individual porphyrins show large changes in d13C and d15N between samples, and an evaluation of how conditions in the basin changed with time through the Miocene would be interesting. Is it a change in species? Changes in nitrate isotopic values? Changes in chlorophyll degradation pathways? Is there any explanation of the difference in the relative isotopic range in the whole photoautotrophic community between Horizons 1 and 2 (Figure 5)?

We in fact speculate that the changes in isotopic values of porphyrins between samples should reflect some change in environmental condition in the basin, or in biological factor influenced by the environment. We did not see any evidence of change in the degradation pathway. Influence of nitrate isotopic value may indeed cause small change in d15N of porphyrins even under largely contribution of N2-fixer, because denitrification in water column in such a oxygen-depleted basin can significantly elevate d15N

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of nitrate. The change in relative isotopic range between two horizons (particularly in d13C) may reflect change in d13C of DIC (in response to the change in oceanic circulation??) or change in the species of primary producer. However, to make a meaningful discussion on these issues, we obviously need more data from many stratigraphic levels, so that we can make much better argument by comparing to other well-studied geological/geochemical data that showed stratigraphic variation responding to some environmental factors. This is obviously one of targets of our future studies.

1. It might be better to refer to "chlorophylls c1-3" rather than just "chlorophylls c".

We changed to refer to "chlorophylls c1-3" on the first appearances in each section.

6. P. 369, line 6; also p. 371, line 7 "Temporally" refers to time. I am unsure whether you mean "temporarily" or "tentatively" instead.

We meant "tentatively", so we changed to "tentatively" in the revised manuscript.

8. P. 377, line 26 Do you mean "denitrification"?

Yes. It was a misspelling.

9. P. 378, line 3 I suggest using an alternate word to "present" as it could be uncertain whether you're referring to your present data set or present-day ocean conditions.

We rephrased as "...relatively 15N-enriched nitrate is likely in this case,...".

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