

***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. Kashiya et al.***

**Anonymous Referee #2**

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Review for MS-NR: bgd-2007-1085; "Reconstruction of the biogeochemistry and ecology of photoautotrophs based on the nitrogen and carbon isotopic compositions of vanadyl porphyrins from Miocene siliceous sediments" Y. Kashiya, N. O. Ogawa, M. Shiro, H. Kitazato, and N. Ohkouchi

**General Comments:**

This paper uses compound-specific stable isotope data from several vanadyl porphyrins to reconstruct the paleoenvironmental water column conditions at the Onna-

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gawa Formation during the Middle Miocene. The authors were able to utilize their previously published methods for porphyrin isolation and identification to isolate a set of porphyrins for various depths. They then used the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of these compounds to determine source compounds, and to conclude that the environment during deposition was greatly influenced by the presence of diazotrophic cyanobacteria, probably in symbiosis with diatoms.

This paper addresses relevant scientific questions within the scope of BG, and provides a new data set in the Authors' continuing research into utilizing porphyrins as paleoenvironmental proxies. Both the title and the abstract summarize the paper well. In general, the methods section is clear and complete, and the data presented support the conclusions drawn. The overall presentation of the paper is good; however there are some sentences that are awkward and confusing (I have listed the some in the technical corrections suggestion). Figures and tables are clear and concise, and the supplementary material is useful. I feel there are a few minor questions brought up by the data that were not answered, but in general I encourage publication of this work.

## Specific comments:

While the paper in general is good and well thought out, I do have a few questions and comments with regards to some of the procedures and conclusions drawn.

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.

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 chloro-

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phyll/chlorophyll products present was proportional to the primary productivity in the lake.

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

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".

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.

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?

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.

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?

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

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values for D13C and D15N also might be useful here.

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.

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?

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).

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

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)?

Technical corrections:

For the most part the language of the paper is good; however, there are a few spots where sentences are awkward and/or unclear.

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

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2. p. 362, lines 11-15 Sentence unclear and awkward.
3. P. 363, line 5 Suggest alternate wording for "long preserved".
4. P. 364, line 18 Missing a period.
5. P. 367, lines 9-12 Sentence unclear and awkward; also, see note in specific comments 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.
7. P. 377, line 1 Add indent at beginning of paragraph.
8. P. 377, line 26 Do you mean "denitrification"?
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.
10. Table 4 is missing a notation regarding Horizon 2.

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