

***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 #1**

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Review of Kashiya et al.

This paper describes the distribution and stable carbon and nitrogen isotopic compositions of porphyrins in the Miocene Onnegawa formation. The authors have isolated a number of porphyrins from several sediments and infer, based on the isotopic compositions and structures, that N<sub>2</sub>-fixing cyanobacteria have been important in the Miocene Pacific Ocean at time of deposition. Furthermore, several different sources are inferred for the different isomers based on cross plots of 13-C and 15-N differences. The work described in this paper forms a nice demonstration of the power of compound specific

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isotope work. The analytical work is excellent and based on methods developed by the authors themselves. The paper is well written and I agree with most of the interpretations of the authors and have only a number of relatively minor comments.

#### General:

- The authors have made similar observations and reached similar conclusions for Cretaceous OAEs. Some discussion on how their Miocene data/interpretation compares with those of Cretaceous OAEs, or at least some reference to it, would have been nice.

- 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.

#### Specific comments:

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

l. 13, p. 362: ....considering that the...

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

l. 17, p. 364: ...relative to cell biomass...

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

l. 3, p. 367: ...in previous studies....

l. 15, p. 367: Use normal font.

l. 2, p. 368 and elsewhere: The compounds were baseline separated and then isolated rather than "baseline isolated"

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.

l. 7, p. 371: Do you mean ..structure tentatively assigned..?

**BGD**

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I. 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.

I. 11, p. 372: ....DPEP (1a) were observed: 3-nor....

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

I. 12-15., p. 375: Unclear to me what you mean. Please rephrase.

I. 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  $^{15}\text{N}$ .

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

I. 11, p. 380: Pancost et al did not look at carboxylases but inferred this to explain the small  $\text{E}_p$ .

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

I. 6, p. 381: Statistically significant ?

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

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

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Interactive comment on Biogeosciences Discuss., 5, 361, 2008.

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